Synthesis of Neutral Molecular Squares Composed of Bis(phosphine)platinum Corner Units and Dialkynyl Linkers. Solid-State Characterization of [Pt(µ-C=CC=C)(dppp)]₄

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Coupling of dichloroplatinum complexes with ethyne or butadiyne, catalyzed by CuI in the presence of Et₂NH, leads to complexes of the types $[Pt(C=CH)_2L_2]$ (L₂ = dppe (1), dppp (2); L = PEt₃ (3)) and $[Pt(C=CC=CH)_2L_2]$ (L₂ = dppp (4), dcpe (5); L = PEt₃ (6)). Attempts to produce tetraplatinum species with ethynyl edges proved unsuccessful, but further coupling of the butadiynylplatinum complexes with $[PtCl_2L_2]$ produces the neutral molecular squares $[Pt(\mu-C=CC=C)_2L_2]_4$ (L₂ = dppp (7), dcpe (8); L = PEt₃ (9)). This two-step approach allows the synthesis of the unsymmetrical complexes $[Pt_2(\mu-C=CC=C)_2(PEt_3)_2L_2]$ (L₂ = dppp (10); dcpe (11)). The molecular structure of 7 reveals that each square has a puckered, butterflylike structure. These pack in a face-to-face manner, generating series of channels that accommodate several solvent molecules. Coupling of *trans*- $[Pt(C=CC=C)_2(PEt_3)_2]$ (6b) with $[PtCl_2L_2]$ (L₂ = dcpe, dppp) leads to complexes assigned as neutral octaplatinum derivatives. The nitrogen-containing complexes $[Pt(C=CC_5H_4N)_2(dppp)]$ (14) and $[Pt(C=CC_6H_4CN)_2-(dppp)]$ (15) react with AgNO₃ to produce Pt₄Ag₄ adducts.

Introduction

The directional bonding approach, advanced separately by Fujita¹ and Stang,² makes use of coordinate bonds in the preparation of a wide range of two- and three-dimensional structures. The basis of this method is that, by selecting suitable corner or angular units and appropriate linker or spacer moieties, two- or three-dimensional structures can be formed by a self-assembly process. A molecular square, for example, may be constructed from four corner units subtending 90° angles, such as a cis square-planar metal center, and four linear linkers.^{3–6}

In the majority of examples reported to date, the products are highly charged. Attempts to reduce such charged species to the corresponding neutral ones have resulted in disintegration of the assemblies.⁷ The availability of neutral macrocycles is highly desirable. They may act as hosts for electron-deficient guests (the presence of many counterions can block the potential cavities in charged macrocyclic structures) and as potential catalytic precursors. In addition, neutral macrocycles, as opposed to their charged analogues, would

(7) Cotton, F. A.; Lin, C.; Murillo, C. A. Inorg. Chem. 2001, 40, 478.

have the advantage of being more soluble in common organic solvents.

Charged palladium- or platinum-containing molecular squares have been prepared using the divalent metals with neutral bidentate ligands at the corners and neutral linkers, giving rise to a 2+ charge per metal center.^{3-6,8-22} Neutral molecular squares, on the other hand, may be accessible either by using neutral bidentate ligands in the corner units and dianionic linkers or by employing dianions at the corners and linking the metal centers by neutral linear units. We chose to pursue the former approach, using alkynyl groups as

- 1996, 15, 904.
 (12) Olenyuk, B.; Whiteford, J. A.; Stang, P. J. J. Am. Chem. Soc.
 1996, 118, 8221.
- (13) Stang, P. J.; Olenyuk, B. Angew. Chem., Int. Ed. Engl. 1996, 35, 732.
- (14) Stang, P. J.; Cao, D. H.; Chen, K.; Gray, G. M.; Muddiman, D. C.; Smith, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 5163.
- (15) Whiteford, J. A.; Lu, C. V.; Stang, P. J. J. Am. Chem. Soc. 1997, 119, 2524.
- (16) Whiteford, J. A.; Stang, P. J.; Huang, S. D. *Inorg. Chem.* **1998**, *37*, 5595.
- (17) Muller, C.; Whiteford, J. A.; Stang, P. J. J. Am. Chem. Soc. 1998, 120, 9827.
- (18) Lee, S. B.; Hwang, S.; Chung, D. S.; Yun, H.; Hong, J. I. *Tetrahedron Lett.* **1998**, *39*, 873.
 (19) Navarro, J. A.; Janik, M. B.; Freisinger, E.; Lippert, B. *Inorg.*
- (19) Navarro, J. A.; Janik, M. B.; Freisinger, E.; Lippert, B. *Inorg. Chem.* **1999**, *38*, 426.
- (20) Schnecbeck, R. D.; Freisinger, E.; Lippert, B. Eur. J. Inorg. Chem. 2000, 1193.
- (21) Wurthner, F.; Sautter, A. Chem. Commun. 2000, 445.

(22) Schweiger, M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. Inorg. Chem. 2002, 41, 2556.

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^{*} To whom correspondence should be addressed. Tel: 314-516-5437. Fax: 314-516-5342. E-mail: ganderson@umsl.edu. (1) Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53 and references therein.

 ⁽¹⁾ Fujita, M. Acc. Chem. Res. 1999, 32, 53 and references therein.
 (2) Leininger, S.; Olenyuk, B.; Stang, P. J. Chem. Rev. 2000, 100, 853 and references therein.

⁽³⁾ Fujita, M.; Yazake, J.; Ogura, K. J. Am. Chem. Soc. 1990, 112, 5645.

⁽⁴⁾ Fujita, M.; Yazake, J.; Ogura, K. Chem. Lett. 1991, 1031.

⁽⁵⁾ Stang, P. J.; Cao, D. H. J. Am. Chem. Soc. 1994, 116, 4981.
(6) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. J. Am. Chem. Soc.

⁽⁶⁾ Stang, P. J.; Cao, D. H.; Saito, S.; Arit, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.

⁽⁸⁾ Stang, P. J.; Whiteford, J. A. Organometallics 1994, 13, 3776.
(9) Rauter, H.; Hillgeris, E. C.; Evxleben, A.; Lippert, B. J. Am. Chem. Soc. 1994, 116, 616.

⁽¹⁰⁾ Fujita, M.; Sasaki, O.; Mitusuhashi, T.; Fujita, T.; Yazake, J.; Yamaguchi, K.; Ogura, K. *J. Chem. Soc., Chem. Commun.* **1996**, 1535. (11) Stang, P. J.; Olenyuk, B.; Fan, J.; Arif, A. M. *Organometallics*

Neutral Molecular Squares

the linkers. Indeed, alkynyl-containing ligands have been used recently in the preparation of a series of selfassembled polygons, ranging from triangles to octagons.²³ Stang has recently reported the use of dicarboxylates in the construction of neutral platinum-containing macrocycles.24

When this work began, there was a report in the literature of the synthesis of the butadiynyl-bridged square $[Pt_4(\mu - C \equiv CC \equiv C)_4(dcpe)_4]$, although it had not been characterized by X-ray crystallography.²⁵ While our work was in progress, a report appeared describing a series of neutral molecular squares of the form $[Pt_4(\mu-C \equiv CC \equiv C)_4L_8]$.²⁶ Whereas the general approach adopted by Bruce and co-workers was similar to ours, there are significant differences both in the synthetic details and in the particular compounds isolated and characterized.

Results and Discussion

Ethynyl Complexes. Alkynylplatinum(II) complexes have been prepared by a variety of methods, including alkynyl transfer from Grignard, organolithium, and organosodium reagents, 2^{7-29} or from less reactive metals, such as tin, mercury, and gold.³⁰⁻³² Base-promoted methods have also been developed, using NaOH, KOH, NH₃, or NHEt₂/Cul.³³⁻³⁷ In attempts to generate bis-(ethynyl)platinum(II) species, we investigated a number of methods, and we found the copper-catalyzed reaction to proceed most smoothly. Thus, treatment of a THF suspension of [PtCl₂(dppe)] with ethyne, in the presence of CuI (10 mol %) and diethylamine, followed by purification, allowed isolation of $[Pt(C \equiv CH)_2(dppe)]$ (1) as a yellow solid in high yield. $[Pt(C \equiv CH)_2(dppp)]$ (2) and *cis*- and *trans*- $[Pt(C \equiv CH)_2(PEt_3)_2]$ (**3a**,**b**) were prepared analogously from [PtCl2(dppp)] and cis- and *trans*-[PtCl₂(PEt₃)₂], respectively (eq 1).

$$L_2 PtCl_2 \xrightarrow{HC=CH} L_2 Pt(C=CH)_2$$
(1)

Complex 1 has been characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography, whereas 2 has been identified by high-resolution mass spectrometry and NMR spectroscopy. The known com-

- (24) Mukherjee, P. S.; Das, N.; Kryschenko, Y. K.; Arif, A. M.; Stang, P. J. J. Am. Chem. Soc. 2004, 126, 2464.
- (25) Al Qaisi, S. M.; Galat, K. J.; Chai, M.; Ray, D. G.; Rinaldi, P. L.; Tessier, C. A.; Youngs, W. J. J. Am. Chem. Soc. 1998, 120, 12149.
- (26) Bruce, M. I.; Costuas, K.; Halet, J.-F.; Hall, B. C.; Low, P. J.; Nicholson, B. K.; Skelton, B. W.; White, A. H. *Dalton* **2002**, 383.
- (27) Bruce, M. I.; Harbourne, D. A.; Waugh, F.; Stone, F. G. A. J. Chem. Soc. 1968, 356
- (28) Bell, R. A.; Chisholm, M. H.; Couch, D. A.; Rankel, L. A. Inorg. Chem. 1977, 16, 677.
- (29) Collamati, I.; Furlani, A. J. Organomet. Chem. 1969, 17, 209. (30) Cardin, C. J.; Cardin, D.; Lappert, M. F. J. Chem. Soc., Dalton Trans. 1977, 767.
- (31) Cross, R. J.; Gemmill, J. J. Chem. Soc., Dalton Trans. 1984, 199 and 205.
- (32) Cross, R. J.; Davidson, M. F. J. Chem. Soc., Dalton Trans. 1986, 411
- (33) Cross, R. J.; Davidson, M. F. J. Chem. Soc., Dalton Trans. 1986, 1987
- (34) Almeida, J. F.; Pidcock, A. J. Organomet. Chem. 1981, 209, 415. (35) Anderson, G. K.; Lumetta, G. J. J. Organomet. Chem. 1985, 295. 257
- (36) Furlani, A.; Licoccia, S.; Russo, M. V. J. Chem. Soc., Dalton Trans. 1984, 2197.
- (37) Cross, R. J.; Davidson, M. F. Inorg. Chim. Acta 1985, 97, L35.



Figure 1. Molecular structure of $[Pt(C=CH)_2(dppe)]$ (1), with atoms represented by thermal ellipsoids at the 50% level.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for $[Pt(C \equiv CH)_2(dppe)]$ (1)

Pt-C(3)	2.025(5)	Pt-C(5)	2.102(5)
Pt-P(1)	2.2851(12)	Pt-P(2)	2.2747(12)
C(3)-C(4)	1.164(8)	C(5)-C(6)	1.184(8)
$\begin{array}{c} C(3)-Pt-C(5)\\ C(3)-Pt-P(2)\\ C(5)-Pt-P(2)\\ Pt-C(3)-C(4) \end{array}$	89.3(2)	C(3)-Pt-P(1)	93.07(14)
	176.80(14)	C(5)-Pt-P(1)	174.13(15)
	92.15(14)	P(1)-Pt-P(2)	85.79(4)
	177.3(5)	Pt-C(5)-C(6)	174.3(5)

plexes 3a,b^{38,39} were characterized by NMR spectroscopy. In each of the four complexes a resonance due to the ethynyl hydrogen is observed between 2.2 and 2.5 ppm, and two ¹³C signals are detected for the ethynyl carbons. The signal due to the β -carbon is the more readily observed (due to the NOE and its shorter relaxation time), and a ²J_{PtC} value of ca. 300 Hz is found in each case. Only in the trans complex **3b** is ${}^{1}J_{\text{PtC}}$ detected, where a value of 485 Hz is found. Each complex exhibits a single resonance in its $^{31}P\{^{1}H\}$ NMR spectrum, with ${}^{1}J_{PtP}$ values in the range 2200–2300 Hz for 1, 2, and 3a, where each P atom lies trans to an ethynyl group, whereas a value of 2368 Hz is found for the mutually trans P atoms in **3b**.

The solid-state structure of 1 has been determined, and its molecular structure is shown in Figure 1. Selected bond distances and bond angles are presented in Table 1. The geometry at platinum is approximately square planar, the sum of the angles around the metal center being 360.4°. The smallest angle (85.79(4)°) is that subtended by the dppe ligand, as anticipated on the basis of its expected bite angle.⁴⁰ The ethynylplatinum units are nearly linear, with the $Pt-C \equiv C$ angles being 174.3(5) and 177.3(5)°. The Pt-C(3) and Pt-C(5) distances are 2.025(5) and 2.012(5) Å, respectively, and the corresponding carbon-carbon distances are 1.164(8) and 1.184(8) Å, as expected for $C \equiv C$ triple bonds.

Attempts to prepare molecular squares with ethynyl edges proved unsuccessful. When 1 or 2 was treated with [PtCl₂(dppe)] or [PtCl₂(dppp)] in the presence of

⁽²³⁾ Jiang, H.; Lin, W. J. Am. Chem. Soc. 2003, 125, 8084.

⁽³⁸⁾ Brooks, E. H.; Glockling, F. J. Chem. Soc. A 1967, 1030.
(39) Sonogashira, K.; Yataki, T.; Tohda, Y.; Takahashi, S.; Hagihara, N. J. Chem. Soc., Chem. Commun. 1971, 291.

⁽⁴⁰⁾ Dierkes, P.; van Leeuwen, P. W. N. M. J. Chem. Soc., Dalton Trans. 1999, 1519.

CuI/Et₂NH in THF solution, no reaction was observed even after refluxing for 4 days. Treatment of 1 or 2 with BuLi, followed by addition of the dichloroplatinum complex, resulted in decomposition. These results may suggest that the ethynyl moiety is too short to allow formation of a stable square, due to the steric repulsions between the phenyl groups that would result. Similarly, whereas reactions of $[M(OTf)_2(dppp)]$ (M = Pd, Pt) with 4,4'-bipyridine were used to generate cationic squares, the analogous reactions with the more compact pyrazine ligand give the monomeric species $[M(C_4H_4N_2)_2(dppp)]$ only.⁴¹ This was attributed to the unfavorable steric interactions that would result if the smaller square were formed. In our case, even with the sterically less demanding PEt₃ ligands in **3a**, coupling with *cis*-[PtCl₂- $(PEt_3)_2$ was unsuccessful.

Butadiynyl Complexes. We next turned our attention to the synthesis of butadiynyl-bridged species. As noted earlier, the preparation of $[Pt_4(\mu-C \equiv CC \equiv C)_4-$ (dcpe)₄] had been described previously.²⁵ During the course of our work, other complexes of the general form $[Pt_4(\mu-C \equiv CC \equiv C)_4L_8]$ were reported by Bruce and coworkers, who prepared the angular units $[Pt(C \equiv CC \equiv$ $(CH)_2L_2$ (L_2 = dppe, dppp; L = PEt₃) by reaction of [PtCl₂L₂] with 1,3-butadiyne in the presence of CuI in DMF/Et₂NH solution.²⁶ We prepared [Pt(C≡CC≡CH)₂L₂] $(L_2 = dppp (4), dcpe (5); L = PEt_3 (6a))$ similarly, but using THF as solvent. We also generated *trans*-[Pt(C≡ $CC \equiv CH_2(PEt_3)_2$] (6b) from *trans*-[PtCl₂(PEt₃)₂]. Complexes 4-6 each exhibit a single ³¹P resonance, with ¹J_{PtP} values of 2200–2300 Hz. In contrast to complexes 1-3, in which the ethynyl hydrogen appears in the range 2.2-2.5 ppm, the butadiynyl hydrogen in complexes **4**–**6** appears between 1.6 and 1.8 ppm. In **6a**,**b**, five-bond couplings to ¹⁹⁵Pt of 9 Hz are observed. Four ¹³C signals are observed for the butadiynyl group in each complex. In 5, for example, resonances are observed at 60.9, 72.8, 93.4, and 99.2 ppm due to the δ -, γ -, β -, and α -carbons, respectively. The two highest frequency signals exhibit coupling to ³¹P, whereas the α -, β -, and γ -carbons each show coupling to ¹⁹⁵Pt, the magnitude of the latter diminishing from 1130 to 311 and then to 36 Hz as the distance from platinum increases. Complexes 4 and 6a proved difficult to isolate in pure form, because decomposition occurred slowly in solution.

We have determined the solid-state structures of **Ga**,**b**; the former was reported by Bruce,²⁶ and so it is not included here. The molecular structure of **Gb** is shown in Figure 2, and selected bond distances and bond angles are given in Table 2. The complex exhibits squareplanar geometry, each of the angles at platinum lying between 89.42(13) and 90.87(13)°. The sum of the angles around platinum is 360.0°. The butadiynyl groups are nearly perfectly linear. The Pt–C distances of 1.995(5) and 2.007(5) Å are similar to those found in **1**. The C–C bond distances reflect the formal bond orders, with short bonds between the α - and β - carbons and γ - and δ -carbons and longer bonds between the β - and γ -carbons.

Neutral Molecular Squares. As described above, treatment of $[PtCl_2L_2]$ with butadiyne in the presence of a catalytic amount of CuI in THF/Et₂NH solution at 0 °C resulted in coupling to produce the angular unit



Figure 2. Molecular structure of *trans*- $[Pt(C=CC=CH)_2$ -(PEt₃)₂] (**6b**), with atoms represented by thermal ellipsoids at the 50% level.

Table 2	2. Se	electe	ed Bor	nd Di	istances	(Å)	and	Bor	ıd
Angles ((deg)	for	trans-	Pt(C	C=CC=C	$H)_2$	(PEt ₃)2] ((6b)

		.(0 00 011)2(1	203721 (00)
Pt(1)-C(1)	2.007(5)	Pt(1)-C(5)	1.995(5)
Pt(1)-P(1)	2.3154(12)	Pt(1)-P(2)	2.3188(12)
C(1)-C(2)	1.202(6)	C(2) - C(3)	1.387(6)
C(3) - C(4)	1.171(7)	C(5)-C(6)	1.211(6)
C(6)-C(7)	1.387(6)	C(7)-C(8)	1.204(7)
C(1)-Pt(1)-C(5)	179.5(2)	C(1)-Pt(1)-P(1)	89.83(13)
C(1) - Pt(1) - P(2)	90.87(13)	C(5) - Pt(1) - P(1)	89.88(13)
C(5) - Pt(1) - P(2)	89.42(13)	P(1) - Pt(1) - P(2)	179.24(5)
Pt(1)-C(1)-C(2)	178.1(4)	C(1)-C(2)-C(3)	178.4(5)
C(2) - C(3) - C(4)	179.1(5)	Pt(1)-C(5)-C(6)	177.2(4)
C(5)-C(6)-C(7)	177.5(5)	C(6) - C(7) - C(8)	178.3(5)



[Pt(C≡CC≡CH)₂L₂] (**4**−**6**). Further reaction of **4**, **5**, or **6a** with the corresponding [PtCl₂L₂] complex at 55 °C for 2 days resulted in formation of the neutral molecular squares [Pt(μ -C≡CC≡C)L₂]₄ (**7**, L₂ = dppp; **8**, L₂ = dcpe; **9**, L = PEt₃) in good yields (Scheme 1). Thus, coupling of the first C−H bond with platinum occurs relatively easily, whereas more forcing conditions are needed to

⁽⁴¹⁾ Stang, P. J.; Cao, D. H. J. Am. Chem. Soc. 1994, 116, 4981.

promote reaction of the second C–H bond. Our results stand in contrast to the report by Bruce and co-workers, who observed that copper-catalyzed coupling of $[PtCl_2L_2]$ with $[Pt(C \equiv CC \equiv CH)_2L_2]$ resulted in polymer formation. They were able to generate the molecular squares from $[Pt(OTf)_2L_2]$ and $[Pt(C \equiv CC \equiv CH)_2L_2]$ in the presence of NaOAc or Et₂NH only under high-dilution conditions.²⁶

Complexes **7**–**9** are off-white, air-stable solids. Each is characterized by a single ³¹P resonance. As expected, no signal corresponding to an alkynyl CH is detected in the ¹H NMR spectrum. Only in the case of **7** could the alkynyl carbons be detected in the ¹³C{¹H} NMR spectrum. Here, the α -carbons appear as a doublet of doublets at 92.0 ppm (²J_{PC} = 146 Hz (trans) and 19 Hz (cis)), although the coupling to ¹⁹⁵Pt could not be determined, whereas the β -carbons exhibit a broad singlet at 96.1 ppm, with ²J_{PtC} = 316 Hz. In complex **4** the α -carbon is more deshielded than the β -carbon, but this trend is reversed in **7**.

Unsymmetrical molecular squares were also obtained in good yield by reaction of *cis*-[Pt(C=CC=CH)₂(PEt₃)₂] with [PtCl₂L₂] under similar conditions. The complexes [Pt₄(μ -C=CC=C)₄(dppp)₂(PEt₃)₄] (**10**) and [Pt₄(μ -C= CC=C)₄(dcpe)₂(PEt₃)₄] (**11**) were isolated as light yellow, air-stable solids. Each exhibited two ³¹P NMR resonances, again with ¹J_{PtP} values between 2200 and 2300 Hz. Attempts to prepare a mixed-metal derivative by reaction of **4** with [PdCl₂(dppp)] were unsuccessful, producing only a black, intractable material. Also, reaction of [PdCl₂(dppp)] with butadiyne produced a dark solid; it may be that diphosphinepalladium species catalyze polymerization of the dialkyne.⁴²

We have found that it is extremely difficult to remove the diethylammonium chloride byproduct from the isolated molecular squares. Signals arising from the Et₂- NH_2^+ cation are always found in their ¹H NMR spectra. Bruce and co-workers noted that when they used Et₂NH as base, the products also contained Et₂NH₂⁺OTf⁻.²⁶ Thus, it has proved impossible to obtain satisfactory elemental analyses for the squares. In addition to NMR spectroscopy, we have used mass spectrometry as a characterization method. The low-resolution FAB mass spectrum of 7 in nitrobenzyl alcohol (NBA) produced the anticipated parent mass envelope centered at m/z 2622 (corresponding to $7 + H^+$), whereas the electrospray mass spectrum contained a cluster centered at m/z 1311 also, due to a doubly charged ion $(7 + 2H^+)$. In both cases, in addition to the expected pattern, a second set of peaks was observed that was shifted to higher mass by 74 mass units, corresponding to the inclusion of one $Et_2NH_2^+$ ion. When CsI was introduced during the measurements, both of the above sets of peaks disappeared, and a new mass envelope was observed centered at m/z 2754, corresponding to 7 + Cs⁺. Thus, the square shows a greater affinity for Cs^+ than for the $Et_2NH_2^+$ cation. Similar behavior was found for complexes 8-11. When 7 was exposed to a solution containing several alkali-metal cations, the intensities of the clusters of peaks in the mass spectrum indicated that its affinity for the ions decreased in the order $Cs^+ > K^+ > Na^+ >$ Li⁺. Complexes 7 and 8 have been characterized satisfactorily by high-resolution mass spectrometry as their Cs⁺ adducts.



Figure 3. Top view of the molecular structure of $[Pt_4(\mu-C=CC=C)_4(dppp)_4]$ (7), with atoms represented by thermal ellipsoids at the 50% level.

It is unclear how the cations are incorporated into the neutral molecular squares, but the fact that they are difficult to remove by extraction and the interactions are maintained under the conditions of mass spectrometry suggests that the interactions are quite strong. It is also uncertain whether the ammonium ions and the alkali-metal ions bind in similar ways. Bruce and coworkers suggested that the N-H bond(s) of the Et₂NH₂⁺ cation may interact with the C≡C bonds of the square.²⁶ That may indeed be the case, and the alkali-metal ions may bind to the triple bonds also. Such "tweezer" interactions are well-known, particularly when Ag⁺ ions are involved.⁴³ It is also possible that the cations interact with the aromatic rings of the dppp ligands, but the incorporation of cations is just as effective in the alkylphosphine-containing complexes, suggesting that this explanation is less likely.

The squares do not crystallize readily. After many unsuccessful attempts, we were able to grow crystals of 7 by slow diffusion of diethyl ether into a chloroform solution. The compound crystallizes in the orthorhombic space group *Ibca*, with eight half-molecules in the asymmetric unit: i.e., four square molecules centered around the inversion center, per unit cell. In addition to 7, the asymmetric unit contains three water molecules, three molecules that we have modeled as acetonitrile, and 1.5 molecules that we have modeled as ethanol. The ethanol would have been present in small amount in the solvents used, but the acetonitrile may have been absorbed adventitiously from the atmosphere or from solutions stored in the same location. A top view of the molecular structure of 7 is shown in Figure 3, and selected bond distances and angles are presented in Table 3. The square consists of four platinum centers at the corners, each coordinated by a chelated dppp ligand and linked by butadiynyl groups. The Pt-C, C=

⁽⁴³⁾ Manna, J.; Kuehl, C. J.; Whiteford, J. A.; Stang, P. J.; Muddiman, D. C.; Hofstadler, S. A.; Smith, R. D. J. Am. Chem. Soc. 1997, 119, 11611.



Figure 4. Side view of $[Pt_4(\mu-C \equiv CC \equiv C)_4(dppp)_4]$ (7), showing the folding of the square to generate a butterfly-shaped unit.

Table 3.	Selected	Bond I	Distances	(Å)	and	Bond
Angle	s (deg) for	r [Pt₄(C	=CC≡C)₄	(dp)	pp)₄l	(7)

Pt(1)-C(1)	2.022(10)	Pt(1)-C(5)	2.007(10)
Pt(1) - P(1)	2.286(2)	Pt(1)-P(2)	2.288(2)
Pt(2)-C(4)	1.993(10)	Pt(2)-C(8#)	2.024(9)
Pt(2)-P(3)	2.281(2)	Pt(2)-P(4)	2.285(3)
C(1)-C(2)	1.191(13)	C(2)-C(3)	1.394(13)
C(3)-C(4)	1.192(13)	C(5)-C(6)	1.194(13)
C(6)-C(7)	1.374(13)	C(7)-C(8)	1.186(12)
	05.0(4)	C(4) D(4) D(4)	00 7(0)
C(1) - Pt(1) - C(5)	85.9(4)	C(I) - Pt(I) - P(I)	92.7(3)
C(1) - Pt(1) - P(2)	171.7(3)	C(5) - Pt(1) - P(1)	178.5(3)
C(5) - Pt(1) - P(2)	85.9(3)	P(1) - Pt(1) - P(2)	95.52(9)
C(4)-Pt(2)-C(8#)	89.5(4)	C(4) - Pt(2) - P(3)	175.0(3)
C(4) - Pt(2) - P(4)	87.3(3)	C(8#)-Pt(2)-P(3)	86.1(2)
C(8#)-Pt(2)-P(4)	176.8(2)	P(3) - Pt(2) - P(4)	97.13(9)
Pt(1)-C(1)-C(2)	174.1(9)	C(1) - C(2) - C(3)	176.5(12)
C(2) - C(3) - C(4)	177.9(11)	C(3) - C(4) - Pt(2)	178.4(10)
Pt(1)-C(5)-C(6)	177.7(9)	C(5) - C(6) - C(7)	178.9(12)
C(6)-C(7)-C(8)	176.5(11)	C(7)-C(8)-Pt(2#)	175.1(8)

C, and C–C distances are similar to those found for 4. The angles at the carbon atoms along the edges range from 174.1 to 178.9(1)°. The geometry at platinum is approximately square planar, the sum of the angles around platinum being 360.0°. The largest angle (95.5°) is that subtended by the dppp ligand. The two P-Pt-C angles differ considerably (85.9 and 92.7°), and the C-Pt-C angle is less than 90°. The separations of the platinum atoms along the edges are 7.775 Å. When the square is viewed from the side, it may be seen to have a puckered, butterfly-like structure. Figure 4 shows a view along one of the Pt…Pt diagonals. Due to the puckered nature of the ring, the diagonal Pt…Pt distances are quite different: namely, 9.973 and 10.725 Å. This differs from the structure of $[Pt(\mu-C \equiv CC \equiv C)-$ (dppe)]₄, reported by Bruce and co-workers, in which the four platinum atoms deviate from the mean plane by only 0.08 Å.26

Consideration of the extended structure reveals some interesting features. The puckered rings do not stack like a series of bowls, as might be expected, but rather they pack in a face-to-face manner, with the tips of the butterfly pointing toward each other. This creates sets of channels, in which the solvent molecules are located. Figure 5 shows the view down the *a* axis, where the puckered squares may be seen to form ladderlike arrays. This results in two distinct types of channels, those between the "rungs" of the ladder and those between the ladders. Water and acetonitrile molecules are located in the channels between the rungs of the ladder, whereas all three types of solvent molecules are found in the channels between the ladders. The view down





Figure 5. Packing diagram for $[Pt_4(\mu-C \equiv CC \equiv C)_4(dppp)_4]$ (7), in a view down the *a* axis.

the *b* axis (not shown) provides another perspective of these same channels. The view along the *c* axis, however, directly on the face of the squares reveals no such features, the squares being offset relative to one another and the aromatic rings of subsequent layers also serving to block the anticipated channels through the centers of the squares. This is in contrast to the dppe analogue where, although the squares are offset slightly relative to one another, the squares do stack and this results in narrow channels running through the centers of the squares.²⁶

Ethynyl Complexes with Nitrogen Donors. We have also used pyridylethynyl and (4-cyanophenyl)ethynyl ligands in the construction of metal-containing arrays. Reaction of [PtCl₂(dppp)] with 4-pyridylethyne in the presence of CuI in THF/Et₂NH solution gave the angular unit $[Pt(C \equiv CC_5H_4N)_2(dppp)]$ (14) in nearly quantitative yield. [Pt(C= $CC_6H_4CN_2(dppp)$] (15) was prepared from [PtCl₂(dppp)] and (4-cyanophenyl)ethyne under similar conditions. Each complex has been characterized by NMR spectroscopy, and 15 has been characterized by elemental analysis and 14 by an X-ray diffraction study. Each complex exhibits a single resonance in its ${}^{31}P{}^{1}H$ NMR spectrum, with a ${}^{1}J_{PtP}$ coupling of about 2200 Hz. The ¹H and ¹³C{¹H} NMR spectra contain the expected numbers of signals. The resonances due to the α -carbons of the alkynyl groups



Figure 6. Molecular structure of $[Pt(C \equiv CC_5H_4N)_2(dppp)]$ (14), with atoms represented by thermal ellipsoids at the 50% level.

Table 4.	Selected H	Bond Distances	(Å) and Bond
Angles	(deg) for [$Pt(C \equiv CC_5H_4N)_2$	(dppp)] (14)

	,		
Pt(1)-C(1)	1.998(2)	Pt(1)-C(8)	2.013(3)
Pt(1)-P(1)	2.2917(6)	Pt(1)-P(2)	2.2959(6)
C(1)-C(2)	1.200(3)	C(2)-C(3)	1.437(3)
C(8)-C(9)	1.180(4)	C(9)-C(10)	1.442(4)
C(1)-Pt(1)-C(8)	86.95(9)	C(1)-Pt(1)-P(1)	177.64(7)
C(1) - Pt(1) - P(2)	90.67(7)	C(8) - Pt(1) - P(1)	90.75(6)
C(8) - Pt(1) - P(2)	177.61(7)	P(1) - Pt(1) - P(2)	91.64(2)
Pt(1)-C(1)-C(2)	179.6(2)	C(1) - C(2) - C(3)	175.0(3)
Pt(1)-C(8)-C(9)	177.5(2)	C(8) - C(9) - C(10)	173.4(3)

in **14** and **15** appear as doublets of doublets at 114.4 and 112.3 ppm, respectively, but couplings to ¹⁹⁵Pt are not observed. The β -carbon signals appear at 106.7 and 109.7 ppm, and a value of ${}^{2}J_{\rm PtC}$ of 335 Hz is found in each case.

The molecular structure of **14** is shown in Figure 6, and selected bond distances and angles are presented in Table 4. The geometry at platinum is approximately square planar, the sum of the angles around the metal center being 360.0°. The C-Pt-C angle is smaller than 90°, and the other three angles are slightly greater than 90°. The alkynylplatinum units are nearly linear. The Pt-C(1) and Pt-C(8) distances are 1.998(2) and 2.013(3) Å, respectively, and the corresponding C=C distances are 1.200(3) and 1.180(4) Å. The Pt-N distances are 7.44 Å. The Pt…N vectors are nearly perpendicular to one another, so this unit represents a suitable corner unit for the construction of metal-containing squares.

Reaction of **14** or **15** with 1 equiv of $AgNO_3$ in MeOH/ MeCN solution produced a light yellow solid that exhibits a single resonance in its ³¹P{¹H} NMR spectrum. In each case the signal is shifted by about 2 ppm to low frequency, and the ¹*J*_{PtP} value is increased by 22 or 46 Hz, respectively. The products are clearly symmetrical in nature, and we propose that they have the octametallic structures [{Pt(C=CC₅H₄N)₂(dppp)}₄Ag₄]-(NO₃)₄ (**16**) and [{Pt(C=CC₆H₄CN)₂-(dppp)}₄Ag₄](NO₃)₄ (**17**). We have been unable to grow crystals of these materials. Although the entire cation does not survive electrospray mass spectrometry, fragments corresponding to one Ag⁺ ligated by two units of **14** or **15** are observed. Since Ag–N bonds are relatively weak, it is not surprising that they should be cleaved under these conditions. Attempts to prepare neutral macrocyclic species using **14** or **15** have proved unsuccessful to date.

Experimental Section

NMR spectra were recorded on a Bruker ARX-500, Varian Unity plus 300, or Bruker Avance 300 spectrometer. ¹H and ¹³C chemical shifts are given relative to the residual solvent resonance; ³¹P chemical shifts are relative to external H_3PO_4 . Positive shifts represent deshielding, and coupling constants are given in hertz. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA.

All reactions were carried out under an atmosphere of argon at ambient temperature, unless specified. All solvents were dried before use. Dichloromethane, methanol, acetonitrile, and diethylamine were distilled from calcium hydride. THF and diethyl ether were distilled from sodium benzophenone ketyl. Complexes **4**, **6a**, **7**, and **9** were prepared by Bruce and coworkers,²⁶ but different experimental methods were used in our work.

Preparation of [Pt(C=CH)₂(dppe)] (1). A suspension of [PtCl₂(dppe)] (0.10 g, 0.15 mmol) in THF (40 mL) and diethylamine (10 mL) was maintained at 0 °C, and CuI (1.5 mg) was added. Ethyne gas was bubbled through the mixture for 2 h, and then the solvent was removed under reduced pressure. The resulting solid was dissolved in CH₂Cl₂ and washed several times with water to remove the metal salts. The organic phase was dried over MgSO4 and filtered. The filtrate was passed through a short column of neutral alumina. The solvent was removed, and the solid was crystallized from CH₂Cl₂/ether. The solid was dried in vacuo, leaving a pale yellow solid (0.080 g, 85%). Anal. Calcd for C₃₀H₂₆P₂Pt: C, 56.00; H, 4.10. Found: C, 55.75; H, 4.20. ¹H NMR (CDCl₃): δ (H) 2.36 (d, ²J_{PH} = 18 Hz, ³J_{PtH} = 21 Hz, PCH₂), 2.54 (d, ⁴J_{PH} = 4 Hz, ³J_{PtH} = 43 Hz, CH), 7.95-7.27 (m, PPh₂). ¹³C{¹H} NMR: δ (C) 28.8 (s, ${}^{2}J_{PtC} = 26$ Hz, P*C*H₂), 97.5 (dd, ${}^{2}J_{PC} = 144$, 15 Hz, Pt*C*), 97.5 (d, ${}^{3}J_{PC} = 34$ Hz, ${}^{2}J_{PtC} = 311$ Hz, PtC=*C*H), 133.7, 131.4, 130.1, 128.9 (PPh₂). ³¹P{¹H} NMR: δ (P) 40.8 (s, ${}^{1}J_{\text{PtP}} = 2288$ Hz). Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of ether into a CH_2Cl_2 solution.

Preparation of [Pt(C≡CH)₂(**dppp)]** (2). This complex was prepared similarly, starting from [PtCl₂(dppp)], and obtained as a pale yellow solid in 87% yield. HRMS (NBA) in FAB mode: calcd for ¹²C₃₁H₂₉P₂¹⁹⁵Pt⁺ (MH⁺), 658.1396; found, 658.1394. ¹H NMR (CDCl₃): δ(H) 2.01 (br, *CH*₂), 2.45 (br, PC*H*₂), 2.21 (d, ⁴*J*_{PH} = 3.6 Hz, ³*J*_{PtH} = 48 Hz, *CH*), 7.74–7.27 (m, *PPh*₂). ¹³C{¹H} NMR: δ(C) 20.5 (s, *CH*₂), 26.3 (s, ²*J*_{PtC} = 36 Hz, *PC*H₂), 95.8 (t, ³*J*_{PC} = 17 Hz, ²*J*_{PtC} = 305 Hz, 2C, PtC≡ *C*H), 97.3 (dd, ²*J*_{PC} = 145, 21 Hz, Pt*C*), 128.3, 130.8, 131.5, 134.0 (*PPh*₂). ³¹P{¹H} NMR: δ(*P*) -6.4 (s, ¹*J*_{PtP} = 2195 Hz).

Preparation of *cis*-[PtC=CH)₂(PEt₃)₂] (3a). This complex was prepared analogously from *cis*-[PtCl₂(PEt₃)₂], and isolated as an off-white solid in 93% yield. ¹H NMR (CDCl₃): *δ*(H) 1.04 (m, *CH*₃), 2.03 (m, PC*H*₂), 2.32 (d, ⁴*J*_{PH} = 3.5 Hz, ³*J*_{PtH} = 48 Hz, *CH*). ¹³C{¹H} NMR: *δ*(C) 8.7 (s, ³*J*_{PtC} = 21 Hz, *C*H₃), 17.0 (m, P*C*H₂), 92.7 (t, ³*J*_{PC} = 16 Hz, ²*J*_{PtC} = 297 Hz, PtC=*C*H), 98.7 (dd, ²*J*_{PC} = 140 Hz, ²*J*_{PC} = 21 Hz, PtC). ³¹P{¹H} NMR: *δ*(P) 4.6 (s, ¹*J*_{PtP} = 2267 Hz).

Preparation of trans-[Pt(C≡CH)₂(**PEt**₃)₂)] (3b). This complex was prepared analogously from *trans*-[PtCl₂(PEt₃)₂] and isolated as a yellow solid in 94% yield. ¹H NMR (CDCl₃): δ (H) 1.20 (m, *CH*₃), 2.14 (m, PC*H*₂). The *CH* signal is obscured by the PCH₂ resonance. ¹³C{¹H} NMR: δ (C) 9.2 (s, ³*J*_{PtC} = 25 Hz, *CH*₃), 16.8 (t, ¹*J*_{PC} = 18 Hz, ²*J*_{PtC} = 72 Hz, P*C*H₂), 95.0 (s, ²*J*_{PtC} = 271 Hz, PtC≡*C*H), 101.4 (t, ²*J*_{PC} = 143 Hz, ¹*J*_{PtC} 485 Hz, Pt*C*). ³¹P{¹H} NMR: δ (P) 11.6 (s, ¹*J*_{PtP} = 2368 Hz).

Preparation of Butadiyne.⁴⁴ KOH (9.0 g, 0.08 mol), water (20.0 mL), and DMSO (5.0 mL) were heated to 70 °C for 30 min in a three-necked flask equipped with a condenser and a dropping funnel. The top of the condenser was connected, via a tube filled with CaCl₂, to a trap containing dry THF, which was cooled to -78 °C. 1,4-Dichloro-2-butyne (4.0 mL, 0.04 mol) was added dropwise over a period of 30 min, while the temperature was maintained at 70 °C. A stream of argon was passed through the apparatus, which forced the butadiyne into the cold THF trap. The THF solution was stored at -45 °C in a sealed container. The weight increase of the trap corresponded to an 80% yield. The material could be stored for at least 3 days without significant deterioration.

Preparation of [Pt(C=CC=CH)2(dppp)] (4). To a suspension of [PtCl₂(dppp)] (0.10 g, 0.15 mmol) in THF (40 mL) and diethylamine (10 mL) was added CuI (1.5 mg). The mixture was maintained at 0 °C, and a cold THF solution (10 mL) of butadiyne was introduced. The reaction mixture was stirred for 2 h at 0 °C, and the solvent was removed under reduced pressure. The resulting solid was dissolved in CH₂Cl₂ and washed several times with water. The organic phase was dried over MgSO₄ and filtered. The filtrate was passed through a short column of neutral alumina. The solvent was removed, and the solid was crystallized from CH₂Cl₂/ether. The solid was dried in vacuo, yielding a pale yellow-brown solid (0.097 g, 95%). Anal. Calcd for C35H28P2Pt: C, 59.57; H, 4.10. Found: C, 58.82; H, 4.26.¹H NMR (CDCl₃): δ(H) 1.6 (s, CH), 2.03 (br, CH₂), 2.50 (br, PCH₂), 7.66–7.26 (m, PPh₂).¹³C{¹H} NMR (DMSO- d_6): δ (C) 19.8 (s, CH₂), 24.4 (m, PCH₂), 65.2 (s, δ -C), 72.8 (s, γ -C), 91.2 (t, ${}^{3}J_{PC} = 16$ Hz, ${}^{2}J_{PtC} = 431$ Hz, β -C), 98.9 $(dd, {}^{2}J_{PC} = 146, 21 Hz, \alpha - C), 129.1, 131.2, 131.7, 134.2 (PPh_2).$ ³¹P{¹H} NMR (CDCl₃): δ (P) -7.1 (s, ¹J_{PtP} = 2200 Hz).

Preparation of [Pt(C=CC=CH)₂(**dcpe)] (5).** This complex was prepared in a similar manner from [PtCl₂(dcpe)] and obtained as a pale yellow solid in 80% yield. Anal. Calcd for C₃₄H₅₀P₂Pt·0.25CH₂Cl₂: C, 55.81; H, 6.91. Found: C, 55.70; H, 6.95. ¹H NMR (CDCl₃): δ (H) 1.12–2.45 (m, C*H* and C*H*₂). ¹³C{¹H} NMR: δ (C) 23.4 (dd, ¹*J*_{PC} = 31 Hz, ¹*J*_{PC} = 10 Hz, ²*J*_{PtC} = 45 Hz, P*C*H), 26.1 (s, *CH*₂), 27.0 (s, ⁴*J*_{PtC} = 22 Hz, *CH*₂), 28.9 (d, ³*J*_{PtC} = 22 Hz, ²*J*_{PtC} = 20 Hz, *CH*₂), 34.7 (d, ¹*J*_{PC} = 31 Hz, ²*J*_{PtC} = 36 Hz, γ -C), 93.4 (d, ³*J*_{PtC} = 31 Hz, ²*J*_{PtC} = 311 Hz, β -C), 99.2 (dd, ²*J*_{PtC} = 136, 15 Hz, ¹*J*_{PtC} = 1130 Hz, α-*C*). ³¹P{¹H} NMR: δ (P) 62.9 (s, ¹*J*_{PtP} = 2273 Hz).

Preparation of *cis*-[Pt(C=CC=CH)₂(PEt₃)₂] (6a). This complex was prepared analogously from *cis*-[PtCl₂(PEt₃)₂] and isolated as an off-white solid in 83% yield. Anal. Calcd for C₂₀H₃₂P₂Pt: C, 45.73; H, 6.09. Found: C, 45.03; H, 5.80. ¹H NMR (CDCl₃): δ (H) 1.13 (m, CH₃), 1.86 (s, ⁵J_{PtH} = 9 Hz, CH), 2.03 (m, PCH₂). ¹³C{¹H} NMR: δ (C) 8.5 (s, ³J_{PtC} = 21 Hz, CH₃), 17.1 (t, ¹J_{PC} = 18 Hz, ²J_{PtC} = 52 Hz, PCH₂), 61.1 (s, δ -C), 72.3 (s, ³J_{PtC} = 38 Hz, γ -C), 88.9 (t, ³J_{PtC} = 1083 Hz, α -C). ³¹P{¹H} NMR: δ (P) 5.7 (s, ¹J_{PtP} = 2270 Hz).

Preparation of *trans*-[**Pt(C**=**CC**=**CH**)₂(**PEt**₃)₂] (**6b**). This complex was prepared similarly from *trans*-[PtCl₂(PEt₃)₂] and obtained as a yellow solid in 87% yield. Anal. Calcd for C₂₀H₃₂P₂Pt: C, 45.73; H, 6.09. Found: C, 45.41; H, 6.17. ¹H NMR (CDCl₃): *δ*(H) 1.17 (m, CH₃), 1.82 (s, ⁵J_{PtH} = 9 Hz, CH), 2.10 (m, PCH₂). ¹³C{¹H} NMR: *δ*(C) 8.4 (s, ³J_{PtC} = 23 Hz, CH₃), 16.4 (t, ¹J_{PC} = 18 Hz, ²J_{PtC} = 70 Hz, PCH₂), 59.8 (s, *δ*-C), 72.3 (s, ³J_{PtC} = 36 Hz, *γ*-C), 91.0 (s, ²J_{PtC} = 287 Hz, *β*-C), 100.1 (t, ²J_{PC} = 15 Hz, ¹J_{PtC} = 1002 Hz, α-C). ³¹P{¹H} NMR: *δ*(P) 13.8 (s, ¹J_{PtP} = 2299 Hz). Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of pentane into a CH₂Cl₂ solution.

Preparation of [Pt(*µ***·C≡CC≡C)(dppp)]**₄ (7). [Pt(dppp)-(C≡CC≡CH)₂] (0.10 g, 0.14 mmol) and [PtCl₂(dppp)] (0.096 g,

0.14 mmol) were stirred in THF (50 mL) and diethylamine (20 mL) in the presence of CuI (2.6 mg) at 55 °C for 2 days. A yellow suspension formed. The solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂, and the resulting solution was washed several times with water. The organic phase was dried over MgSO₄ and filtered. The filtrate was passed through a short column of neutral alumina. The solvent was removed, and the solid was crystallized from CH₂Cl₂/ether. The solid was dried in vacuo, yielding an offwhite solid (0.14 g, 78%). HRMS (NBA, CsI) in FAB mode: calcd for ${}^{12}C_{124}H_{104}P_8{}^{195}Pt_4Cs^+$ (M + Cs⁺), 2753.3658; found, 2753.3638. ¹H NMR (CDCl₃): δ(H) 1.93 (br, CH₂), 2.37 (br, PCH₂), 7.07–7.62 (m, PPh₂). ¹³C{¹H} NMR (DMSO- d_6): δ (C) 18.8 (s, CH_2), 24.1 (m, PCH_2), 92.0 (dd, ${}^2J_{PC} = 146$ Hz, ${}^2J_{PC} =$ 19 Hz, Pt*C*), 96.1 (br, ${}^{2}J_{PtC} = 316$ Hz, PtC=*C*), 127.6, 130.3, 132.1, 134.5 (PPh₂).³¹P{¹H} NMR: δ (P) -8.5 (s, ¹J_{PtP} = 2202 Hz). Crystals suitable for an X-ray diffraction study were grown from a CHCl₃/Et₂O/MeCN mixture.

Preparation of [Pt(μ -C=CC=C)(dcpe)]₄ (8). This complex was prepared in a similar manner from [Pt(dcpe)(C=CC=CH)₂] and [PtCl₂(dcpe)] and isolated as a brown solid in 86% yield. HRMS (NBA, CsI) in FAB mode: Calcd for ¹²C₁₂₀H₁₉₂P₈-¹⁹⁵Pt₄Cs⁺ (M + Cs⁺), 2794.0569; found, 2794.0464. ¹H NMR (CDCl₃): δ (H) 1.12–2.45 (m, *CH* and *CH*₂). ³¹P{¹H} NMR: δ -(*P*) 62.6 (s, ¹*J*_{PtP} = 2288 Hz).

Preparation of [Pt(μ-C≡CC≡C)(PEt₃)₂]₄ (9). This complex was prepared in a similar manner from *cis*-[Pt(PEt₃)₂·(C≡CC=CH)₂] and *cis*-[PtCl₂(PEt₃)₂] and obtained as an off-white solid in 77% yield. LRMS in ESI⁺ mode, *m/z* (relative intensity calculated, observed) for C₆₄H₁₂₀P₈Pt₄Cs⁺ (MCs⁺): 2046 (20, 24), 2047 (47, 49), 2048 (77, 79), 2049 (98, 96), 2050 (100, 100), 2051 (87, 92), 2052 (66, 72), 2053 (46, 50), 2054 (28, 33). ¹H NMR (CDCl₃): *δ*(H) 1.14 (m, *CH*₃), 2.06 (m, PC*H*₂). ³¹P{¹H</sup>} NMR: *δ*(P) 6.4 (s, ¹*J*_{PtP} = 2318 Hz).

Preparation of [Pt₄(μ -C=CC=C)₄(**dppp**)₂(**PEt**₃)₄] (10). This complex was prepared in a similar manner from *cis*-[Pt-(PEt₃)₂(C=CC=CH)₂] and [PtCl₂(dppp)]. It was obtained as a light yellow solid in 82% yield. ¹H NMR (CDCl₃): δ (H) 1.12–2.41 (m, *CH*₂ and *CH*₃), 7.02–7.68 (m, P*Ph*₂). ³¹P{¹H} NMR: δ (P) 6.3 (s, ¹J_{PtP} = 2284 Hz, PEt₃), -6.7 (s, ¹J_{PtP} = 2208 Hz, dppp).

Preparation of [Pt₄(*μ*-**C**=**C**C=**C**)₄(**dcpe**)₂(**PEt**₃)₄] (11). This complex was prepared in a similar manner from *cis*-[Pt-(PEt₃)₂(C=CC=CH)₂] and [PtCl₂(dcpe)]. It was obtained as a light yellow solid in 82% yield. LRMS in ESI⁺ mode, *m*/*z* (relative intensity calculated, observed) for C₉₂H₁₅₆P₈Pt₄Cs⁺ (MCs⁺): 2420 (69, 70), 2421 (92, 90), 2422 (100, 100) 2423 (92, 90), 2424 (73, 80), 2425 (52,59). ¹H NMR (CDCl₃): *δ*(*H*) 1.07− 2.45 (m, *CH*, *CH*₂ and *CH*₃). ³¹P{¹H} NMR: *δ*(*P*) 5.3 (s, ¹*J*_{PtP} = 2282 Hz, PEt₃), 62.4 (s, ¹*J*_{PtP} = 2292 Hz, dcpe).

Preparation of [Pt₂(μ -C=CC=C)₂(dcpe)(PEt₃)₂]₄ (12). [PtCl₂(dcpe)] (0.10 g, 0.15 mmol) and *trans*-[Pt(PEt₃)₂(C=CC= CH)₂] (0.076 g, 0.15 mmol) were stirred in THF (50 mL) and diethylamine (20 mL) in the presence of CuI (2.6 mg) at 55 °C for 2 days. A yellow suspension formed. The solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and washed several times with water. The organic phase was dried over MgSO₄ and filtered. The filtrate was passed through a short column of neutral alumina. The solvent was removed, and the solid was crystallized from CH₂Cl₂/ether, yielding a yellow solid (0.146 g, 87%). ¹H NMR (CDCl₃): δ (H) 1.13–2.35 (m, CH, CH₂, and CH₃). ³¹P{¹H} NMR: δ (P) 12.3 (s, ¹J_{PtP} = 2338 Hz, PEt₃), 62.0 (s, ¹J_{PtP} = 2329 Hz, dcpe).

Preparation of [Pt₂(μ -C=CC=C)₂(**dppp**)(PEt₃)₂]₄ (13). This complex was prepared in a similar manner from *trans*-[Pt(PEt₃)₂(C=CC=CH)₂] and [PtCl₂(dppp)]. The product was obtained as a light yellow solid (0.19 g, 82%). ¹H NMR (CDCl₃): δ (H) 1.07–2.45 (m, CH₂ and CH₃). ³¹P{¹H} NMR: δ (P) 13.7 (s, ¹J_{PtP} = 2368 Hz, PEt₃), -6.7 (s, ¹J_{PtP} = 2212 Hz, dppp).

⁽⁴⁴⁾ Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: New York, 1988; p 179.

Table 5. Crystal Data and Structure Refinement Details for $[Pt(C=CH)_2(dppe)]$ (1),	
<i>trans</i> $[Pt(C \equiv CC \equiv CH)_2(PEt_3)_2]$ (6b), $[Pt_4(C \equiv CC \equiv C)_4(dppp)_4]$ (7), and $[Pt(C \equiv CC_5H_4N)_2(dppp)]$ (1)	14)

	$\begin{array}{c} Pt(C \equiv CH)_2(dppe) \\ (1) \end{array}$	$Pt(C \equiv CC \equiv CH)_2(PEt_3)_2$ (6b)	$\begin{array}{c} Pt_4(C \equiv CC \equiv C)_4(dppp)_4 \\ (7) \end{array}$	$\begin{array}{c} Pt(C \equiv CC_5H_4N)_2(dppp) \\ (14) \end{array}$
cryst syst	monoclinic	orthorhombic	orthorhombic	triclinic
space group, Z	$P2_1/n, 4$	$Pna2_1, 4$	Ibca, 8	$P\overline{1}$, 2
a, Å	9.2339(1)	16.6199(5)	19.9283(3)	10.5896(2)
<i>b</i> , Å	13.7662(2)	7.2620(2)	33.6486(5)	13.0367(2)
<i>c</i> , Å	19.8834(3)	17.6231(5)	43.7364(8)	14.1702(3)
α, deg	90	90	90	67.352(1)
β , deg	93.027(1)	90	90	75.040(1)
γ , deg	90	90	90	79.537(1)
V, Å ³	2523.97(6)	2127.00(11)	29 327.9(8)	1736.78(6)
density (calcd), Mg/m ³	1.694	1.653	1.411	1.552
temp, K	218(2)	170(2)	120(2)	223(2)
abs coeff, mm^{-1}	5.702	6.746	3.946	4.163
<i>F</i> (000)	1256	1040	12 400	804
θ range, deg	2.05 - 27.00	2.31-30.01	1.86 - 26.00	1.70 - 28.00
no. of rflns collected	57 794	50 454	201 666	3 270
no. of indep rflns	5516 ($R_{\rm int} = 0.031$)	5879 ($R_{\rm int} = 0.0252$)	14 413 ($R_{\rm int} = 0.1005$)	8288 ($R_{\rm int} = 0.022$)
abs cor	empirical	empirical	empirical	empirical
no. of data/restraints/params	5516/3/310	5879/1/208	14 413/0/760	8288/0/415
goodness of fit on F^2	1.239	0.928	1.144	1.129
final <i>R</i> indices $(F^2 > 2.0\sigma(F^2))$: $R(F), R_w(F^2)$	0.026, 0.072	0.022, 0.054	0.062, 0.187	0.022, 0.043
largest diff peak and hole, e ${\rm \AA}^{-3}$	0.94, -0.87	3.74, -1.15	2.96, -1.57	0.82, -0.75

Preparation of 4-HC≡CC₅H₄N. 4-Bromopyridine hydrochloride (2.0 g, 10.3 mmol) and diethylamine (20 mL) were stirred overnight in THF (50 mL) in the absence of light to obtain free 4-bromopyridine. HC≡CSi(CH₃)₃ (1.5 mL, 10.6 mmol), CuI (0.04 g), and [PdCl₂(PPh₃)₂] (0.14 g) were added, and the reaction mixture was stirred overnight in the absence of light. The solvent was removed under reduced pressure. The residue was extracted several times with diethyl ether, and the ether extracts were passed through neutral alumina. The solvent was removed to afford 4-((trimethylsilyl)ethynyl)pyridine. Desilylation of this material was achieved by treatment with 2.0 N NaOH (2.0 mL) in methanol (30 mL) at room temperature for 2 h. Removal of the solvent under reduced pressure and purification by chromatography on alumina, with hexane/benzene as eluent (3/2), resulted in isolation of a light yellow solid (0.52 g, 50% overall yield). 4-(CH₃)₃SiC≡CC₅H₄N: ¹H NMR (CDCl₃) δ (H) 0.25 (s, CH₃) 7.04 (d, ³J_{HH} = 6 Hz, CH), 8.28 (d, ${}^{3}J_{\text{HH}} = 6$ Hz, CH); ${}^{13}C{}^{1}H$ NMR $\delta(C) -0.2$ (s, CH₃), 100.2, 102.0 (C=C), 126.0 (CH), 149.8 (CH), 131.4 (s, ipso C). 4-HC=CC₅H₄N: ¹H NMR (CDCl₃) δ (H) 3.31 (s, C=CH), 7.37 (d, ${}^{3}J_{\text{HH}} = 6$ Hz, CH), 8.61 (d, ${}^{3}J_{\text{HH}} = 6$ Hz, CH); ${}^{13}C{}^{1}H$ NMR δ(C) 81.3 (C=CH), 82.3 (C=CH), 130.7 (s, *ipso C*), 126.5 (CH), 150.2 (CH).

Preparation of 4-HC=**CC**₆**H**₄**CN.** This ligand was prepared in a similar manner from 4-bromobenzonitrile, HC=CSi-(CH₃)₃, CuI, and [PdCl₂(PPh₃)₂], followed by desilylation with NaOH in methanol, and isolated in a 75% overall yield. 4-(CH₃)₃SiC=CC₆H₄CN: ¹H NMR (CDCl₃) δ (H) 0.07 (s, *CH*₃), 7.37 (*CH*); ¹³C{¹H} NMR δ (C) 0.1 (s, *C*H₃), 100.0, 103.4 (*C*= *C*), 112.1 (*C*N), 118.8 (*C*H), 128.4 (*ipso C*), 132.3 (*ipso C*), 132.8 (*C*H). 4-HC=CC₆H₄CN: ¹H NMR (CDCl₃) δ (H) 3.9 (s, *CH*) 7.51 (*CH*); ¹³C{¹H} NMR δ (C) 79.4 (*C*=CH), 81.7 (C=*C*H), 112.4 (*C*N), 118.4 (*ipso C*), 127.1 (*C*H), 132.1 (*ipso C*), 132.8 (*C*H).

Preparation of [Pt(C=CC₅H₄N)₂(dppp)] (14).⁴¹ A suspension of [PtCl₂(dppp)] (0.10 g, 0.15 mmol) and 4-HC= CC₅H₄N (0.031 g, 0.30 mmol) in THF (40 mL) and diethylamine (10 mL) was maintained at 0 °C, and CuI (1.5 mg) was added. The reaction mixture was stirred for 2 h at 0 °C, and the solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and washed several times with water. The organic phase was dried over MgSO₄ and filtered. The filtrate was passed through a short column of neutral alumina. The solvent was removed, and the solid was crystallized from CH₂Cl₂/ether, yielding a yellow solid (0.116 g, 96%). ¹H NMR (CDCl₃): δ (H) 2.09 (m, *CH*₂), 2.56 (m, PCH₂), 6.67 (br, C₅H₄N), 7.27–7.73 (m, *PPh*₂), 8.23 (br, C₅H₄N). ¹³C{¹H} NMR: δ (C) 19.2

(s, *C*H₂), 26.3 (m, *PC*H₂), 114.4 (dd, ${}^{2}J_{PC} = 124$ Hz, ${}^{2}J_{PC} = 21$ Hz, Pt*C*), 106.7 (t, ${}^{3}J_{PC} = 17$ Hz, ${}^{2}J_{PtC} = 335$ Hz, Pt*C*=*C*), 125.7, 129.0, 131.2, 131.6, 134.0, 135.7, 149.4 (C_{5} H₄N, *PPh*₂). ${}^{31}P{}^{1}$ H} NMR: δ (*P*) -5.6 (s, ${}^{1}J_{PtP} = 2198$ Hz). Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a CH₂Cl₂/Et₂O solution.

Preparation of [Pt(C≡CC₆H₄CN)₂(dppp)] (15). This complex was prepared similarly from [PtCl₂(dppp)] and 4-HC≡ CC₆H₄CN and obtained as a yellow solid (0.122 g, 95%). Anal. Calcd for C₄₅H₃₄P₂NPt·CH₂Cl₂: C, 58.48; H, 3.84. Found: C, 58.47; H, 3.64. ¹H NMR (CDCl₃): δ(H) 2.11 (br, CH₂), 2.56 (br, PCH₂), 6.82–7.74 (m, C₅H₄N, PPh₂). ¹³C{¹H} NMR: δ(C) 20.2 (s, CH₂), 26.1 (m, PCH₂), 112.3 (dd, ²J_{PC} = 146 Hz, ²J_{PC} = 21 Hz, PtC), 109.7 (t, ³J_{PC} = 17 Hz, ²J_{PtC} = 335 Hz, PtC≡C), 108.1 (CN), 119.7, 128.6, 130.6, 131.0, 131.2, 131.9, 133.0, 133.7 (C₆H₄, PPh₂). ³¹P{¹H} NMR: δ(P) −5.5 (s, ¹J_{PtP} = 2192 Hz).

Preparation of [Pt₄(\mu-C=C₅H₄N)₈(dppp)₄Ag₄](NO₃)₄ (**16**). [Pt(C=CC₅H₄N)₂(dppp)] (0.10 g, 0.12 mmol) and AgNO₃ (0.02 g, 0.12 mmol) were dissolved in MeOH/CH₃CN (1:1, 20 mL) and stirred overnight in the absence of light. The solvents were removed, and the resulting solid was crystallized from CH₂Cl₂/ether, yielding a light yellow solid, which was dried in vacuo (0.098 g, 81%). LRMS in ESI⁺ mode, *m*/*z* (relative intensity calculated, observed) for C₈₂H₆₈P₄N₄Pt₂Ag: 1728 (37, 35), 1729 (70, 67), 1730 (92, 92), 1731 (100, 100), 1732 (84, 89), 1733 (60, 64), 1734 (36, 38). ¹H NMR (CDCl₃): δ (H) 2.07 (br, *CH*₂), 2.67 (br, PC*H*₂), 6.60–7.63 (m, C₅*H*₄, P*Ph*₂). ³¹P{¹H} NMR: δ (P) –7.5 (s, ¹*J*_{PtP} = 2320 Hz).

Preparation of [Pt₄(μ -C=CC₆H₄CN)₈(**dppp**)₄Ag₄](NO₃)₄ (17). This complex was prepared similarly from [Pt(C=CC₆H₄-CN)₂(dppp)] and AgNO₃ and obtained as a light yellow solid in 78% yield. LRMS in ESI⁺ mode, m/z (relative intensity calculated, observed) for C₉₀H₆₈P₄N₄Pt₂Ag: 1824 (35, 34), 1825 (68, 68), 1826 (91, 94), 1827 (100, 100), 1828 (86, 90), 1829 (63, 66), 1830 (38, 42). ¹H NMR (CDCl₃): δ (H) 2.25 (br, CH₂), 2.68 (br, PCH₂), 6.67–7.63 (m, C₆H₄, PPh₂). ³¹P{¹H} NMR: δ (P) –8.2 (s, ¹J_{PtP} = 2338 Hz).

X-ray Structure Determinations. Preliminary examination and data collection were performed using a Bruker SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source (40 kV × 50 mA) using graphite-monochromated Mo K α radiation (λ = 0.710 73 Å). Preliminary unit cell constants were determined with a set of 45 narrow-frame (0.3° in ω) scans. The doublepass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT was used for frame integration.⁴⁵ Final cell constants were determined by a global refinement of *xyz* centroids of reflections harvested from the entire data set. An empirical absorption correction was applied using equivalent reflections (SAD-ABS).⁴⁶ Structure solution and refinement were carried out using the SHELXTL-PLUS software package.⁴⁷ The absolute structure of **6b** was determined using the Flack parameter *x* = 0.1(1). Crystallographic data are collected in Table 5.

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Supporting Information Available: Tables of crystal data, atomic coordinates and displacement parameters, and all bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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⁽⁴⁵⁾ SMART and SAINT; Bruker Analytical X-ray Division, Madison, WI, 2002.

⁽⁴⁶⁾ SADABS: Blessing, R. H. Acta Crystallogr., Sect. A **1995**, *51*, 33.

⁽⁴⁷⁾ Sheldrick, G. M. SHELXTL-PLUS Software Package; Bruker Analytical X-ray Division, Madison, WI, 2002.