Synthesis and Reactivity of Platinum Complexes of Cyclic Alkynes and Tropynes

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Platinum complexes of dibenzannelated didehydrotropone 5, didehydrooxepin 6, and didehydrocycloheptatriene 7 have been synthesized in good yields by base-induced dehydrobromination from the corresponding bromoalkenes in the presence of $Pt(PPh_3)_3$. Complex **5** crystallizes in triclinic space group $P\overline{1}$: a = 11.221(2) Å, b = 11.318(2) Å, c = 16.621(4) Å, $\alpha = 74.22(2)^{\circ}, \beta = 78.86(2)^{\circ}, \gamma = 73.56(2)^{\circ}, V = 2445.0(9)$ Å³, Z = 2, R = 5.79%. Reaction of 5 with tert-butyl isocyanide gives a single phosphine displacement product 11, and reaction with HBF_4 and HBr gives oxidative addition products 8 and 12, respectively. Bis-(dicyclohexylphosphino)ethane displaces triphenylphosphine from 5 and 6 to give 9 and 10. Complex 5 reacts with tetracyanoethylene to give the highly distorted substituted benzene 14 which was characterized by X-ray diffraction. Crystal data for 14: Space group $P\overline{1}$, a =11.274(2) Å , b = 11.826(1) Å, c = 13.474(2) Å, $\alpha = 111.79(1)^{\circ}, \beta = 106.34(1)^{\circ}, \gamma = 98.54(1)^{\circ}, \beta = 106.34(1)^{\circ}, \gamma = 106.34(1)^{\circ}, \beta = 106.34(1)^{\circ}, \gamma = 106.34(1)^{\circ}$ V = 1534.9(4) Å³, Z = 2, R = 6.17%. Complex 6 reacts with TCNE to give the platinacyclopent-2-ene 15 (55%). Complex 15 crystallizes in monoclinic space group Ia: a = 17.175(3) Å, b = 15.411(2) Å, c = 18.661(2) Å, $\beta = 91.86(1)^{\circ}$, V = 4915(2) Å³, R = 4.74%. Reaction of 7 with triphenylcarbenium tetrafluoroborate gives the dibenzannelated tropyne complex 16 which can be converted back to 7 with $KBEt_3H$. Reaction of 16 with bis(dicyclohexylphosphino)ethane gives 17 (60%), and reaction with HBr gives the oxidative addition product 18 which slowly isomerizes to 19.

Introduction

We recently reported the synthesis and characterization of platinum¹ (1) and zirconium² (2) complexes of



tropyne by hydride abstraction from the corresponding complexes of cycloheptadieneyne. By analogy with wellestablished chemistry of tropones, it occurred to us that, in principle, it should be possible to prepare alkoxy- and hydroxy-substituted tropyne complexes by alkylation or protonation of didehydrotropone complexes.³



To test this hypothesis, preparation of a metal complex of didehydrotropone was considered. However, synthesis of appropriate starting materials was formidable. We therefore decided to focus initially on the much more readily available dibenzannelated analogue 5 (Scheme 1). At this time we report the successful synthesis of 5 which, although it could be neither alkylated nor protonated on the carbonyl oxygen, underwent reaction with TCNE to give the highly cluttered and distorted benzene derivative 14 (Scheme 3). This surprising result induced us to prepare platinum complexes of two other dibenzannelated cycloheptadienynes (6 and 7), and although neither underwent trimerization when treated with TCNE, one (6) underwent a rare coupling to form 15 (Scheme 3) and the other (7), upon hydride abstraction, gave the new tropyne complex 16 (Scheme 4).

Results and Discussion

Preparation of Platinum Alkyne Complexes. Dibenzannelated didehvdrotropone 5, didehvdrooxepin 6, and didehydrocycloheptatriene 7 have been synthesized from the corresponding bromoalkenes as shown in Scheme 1. After workup yellow (5, 6) and off-white (7) crystalline solids were obtained in 60-75% yield. All new complexes were characterized by ¹H, ¹³C, ³¹P, and ¹⁹⁵Pt NMR (Table 2), HRMS, and elemental analysis. The proton NMR spectrum of these complexes is somewhat surprising in that the chemical shifts of the protons nearest the triple bond (H1) are in the range 5.8-6.5 ppm which is uncommonly high field for aromatic compounds. This upfield shift was shown in two ways to be due to diamagnetic shielding by triphenylphosphine coordinated to the platinum. First, in an NOE study of 6, irradiation of the ortho protons of triphenylphosphine led to an 11.9% enhancement of H1. Second, analogues of 5 and 6 that are incapable of significant shielding (9, 10) were prepared by ligand

⁸ Abstract published in Advance ACS Abstracts, April 15, 1995. (1) Lu, Z.; Abboud, K. A.; Jones, W. M. J. Am. Chem. Soc. 1992, 114, 10991.

⁽²⁾ Lu, Z.; Jones, W. M. Organometallics 1994, 13, 1539.

⁽³⁾ Douglas, L. Non-Benzenoid Conjugated Carbocyclic Compounds; Elsevier Science Publishers: Amsterdam, 1984.

Scheme 1



exchange and their spectra compared with **5** and **6**. All aromatic resonances appear below 7 ppm.⁴ The infrared spectra of the alkyne complexes **5**, **6**, and **7** showed the expected alkyne absorptions at 1708, 1691, and 1689 cm⁻¹, respectively. These are in the range normally expected for platinum alkyne complexes (1630-1780 cm⁻¹) and are at a lower frequency than those of the corresponding complexes of cycloheptyne (1771 cm⁻¹) and cyclohexyne⁵ (1721 cm⁻¹) as would be expected from conjugation with the aryl rings.

X-ray Crystal Structure of 5. Crystals of 5 were obtained from a mixture of toluene and hexane as yellow plates. Complex 5 crystallizes in the P1 space group together with one molecules of toluene which is disordered in two different positions. A thermal ellipsoid drawing of the structure is given in Figure 1, while crystal data are listed in Table 5. Selected bond lengths and angles and final fractional atomic coordinates are provided in Tables 1 and 6, respectively. The alkyne bond length in 5 is 1.283(15) Å and is equal, within experimental error, to that in platinum complexes of cyclohexyne and cycloheptyne.⁶ The alkyne ligand is bent, with a dihedral angle between the phenyls of $146.8(5)^{\circ}$. This value is almost the same as in dibenzotropone⁷ [142.8(6)°]; coordination of platinum has virtually no effect on the geometry of the ligand. Complexes of this type have an essentially square planar geometry with the donor phosphine groups occupying *cis* coordination sites. The coordinated alkyne is slightly rotated from the P1-Pt-P2 planes. In complex 5 the dihedral angle between planes defined by Pt, P1, P2 and Pt, C10, C11 is 12.3(7)° and is one of the largest among all known platinum alkyne complexes.6

Reactions of Alkyne Complexes. Some reactions of the alkyne complexes 5-7 are summarized in Scheme 2. Overall, the reactivity of these complexes is quite moderate. They show no reaction with weak acids such as ethanol and acetonitrile even when warmed to 80 °C for 2 days. They also show no reaction with methyl iodide, dimethyl acetylenedicarboxylate or phenylacety-



Figure 1. Structure and labeling scheme for **5** with 40% probability of thermal ellipsoids.

Table 1.	Selected Bond Lengths (Å) and Angles	5
	(deg) for Complex 5	

	Bond Lengths (Å)					
Pt-P1	2.290(3)	P2-C21	1.840(11)			
Pt-P2	2.277(3)	P2-C31	1.836(12)			
Pt-C10	2.056(13)	P2-C41	1.826(11)			
Pt-C11	2.031(13)	C5-O	1.27(2)			
P1-C51	1.839(11)	C11-C10	1.283(15)			
P1-C61	1.826(10)	C14-C10	1.42(2)			
P1-C71	1.844(13)	C12-C11	1.43(2)			
	Bond Angles (deg)					
P1-Pt-P2	102.04(12)	C13-C5-O	115.7(13)			
P1-Pt -C10	144.4(3)	C15 - C5 - O	116.3(13)			
P2-Pt -C10	113.0(3)	C11-C10-C14	135.8(14)			
P2-Pt-C11	148.9(3)	C14-C10-Pt	152.3(10)			
C10-Pt-C11	36.6(4)	C12-C11-Pt	154.1(8)			
C11-Pt-P1	109.0(3)	Pt-C11-C10	72.8(8)			

lene. Attempts to protonate 5 on the carbonyl oxygen to give the hydroxytropyne complex also failed; as Bennett observed for an analogous complex of cyclohexyne,⁵ the electrophile apparently attacks the metal which leads to the σ complexes 8 and 12 from HBF₄ and HBr, respectively. As mentioned above, complexes 5 and 6 react readily with bis(dicyclohexylphosphino)ethane to give 9 and $10^{5,8}$ The carbon-carbon triple bond in 9 shows a red shift of 18 cm^{-1} as compared with 6 which could be expected from the increased basicity of the phosphine ligand. However, the frequency of the same bond in 10 is almost identical to that of 5. Complex 5 also reacted rapidly with tert-butyl isocyanide to give 11 in good yield; further ligand exchange or other reactions could not be induced, even at elevated temperature. The IR of 11 shows bands at 1710.9 and 2155.5 cm^{-1} due to the coordinated triple bond and the isocyanide ligand, respectively. The $^{195}Pt{^1H}$ spectrum shows a signal at -4694 ppm as a broad doublet which is a result of coupling to one phosphine and ^{14}N .

Bennett has found that TCNE reacts with bis(triphenylphosphine)platinum complexes of cyclohexyne and cycloheptyne to give the bis(triphenylphosphine)-plat-

⁽⁴⁾ For a recent similar effect in organometallic complexes see: Seino, H.; Ishii, Y.; Hidai, M. J. Am. Chem. Soc. **1994**, *116*, 7433. (5) Rompatt M. A.; Vachida, T. J. Am. Chem. Soc. **1975**, *100*, 1750.

⁽⁵⁾ Bennett, M. A.; Yoshida, T. J. Am. Chem. Soc. 1978, 100, 1750.
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(7) Oddon, P. Y.; Darbon, N.; Reboul, J. P.; Cristau, B.; Soyfer, J.

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complex no.	$^{195}Pt\{^{1}H\}$ (ppm)	$^{31}P{^{1}H} (ppm)$	
5	$-4745.2 (t, {}^{1}J_{Pt-P} = 3391.4 \text{ Hz})$	23.73 (s)	
6	-4749.6 (t, ${}^{1}J_{\text{Pt-P}} = 3418.3$ Hz)	23.75 (s)	
7	-4732.4 (t, ${}^{1}J_{\text{Pt-P}} = 3385.7$ Hz)	24.42(s)	
8	-4071.8 (t, ${}^{1}J_{\text{Pt}-\text{P}} = 3137.6$ Hz)	24 (s)	
9	-5101.5 (t, ${}^{1}J_{\text{Pt-P}} = 3056$ Hz)	69.29 (s)	
10	-5047.9 (t, ${}^{1}J_{\text{Pt-P}} = 3010.4$ Hz)	68.03 (s)	
11	-4694 (d, br, ${}^{1}J_{Pt-P} = 3196.4$ Hz)	25.99 (s)	
12	$-4554.3 (dd, {}^{1}J_{Pt-P1} = 1686.2 Hz, {}^{1}J_{Pt-P2} = 4432.2 Hz)$	15.2 (d, ${}^{2}J_{P-P} = 15.4$, P2), 16.77 (d, ${}^{2}J_{P-P} = 15.4$, P1)	
13	$-4868 (t, {}^{1}J_{Pt-P} = 3743 \text{ Hz})$	16.03 (s)	
13a	-5257.3 (t, ${}^{1}J_{\text{Pt-P}} = 3310$ Hz)	67.2 (s)	
15	$-4347.3 (dd, {}^{1}J_{Pt-P1} = 3259.4 Hz, {}^{1}J_{Pt-P2} = 1918.2 Hz)$	13.68 (d, ${}^{2}J_{P-P} = 20.5 \text{ Hz}$), 14.57 (d, ${}^{2}J_{P-P} = 20.5$)	
16	-4060.2 (t, ${}^{1}J_{Pt-P} = 3189.2$ Hz)	19.96 (s)	
20	-5257.3 (t, ${}^{1}J_{Pt-P} = 3310$ Hz)	67.2 (s)	
17	-4733.4 (t, ${}^{1}J_{\text{Pt-P}} = 3366.6$ Hz)	$21.95 (s, PPh_3), 34.93 (s, PCy_2)$	
18	$-4434.8 (dd, {}^{1}J_{Pt-P} = 849 \mathrm{Hz}, {}^{1}J_{Pt-P2} = 4121 \mathrm{Hz})$	13.96 (d, ${}^{2}J_{P-P} = 18$ Hz, P1), 15.03 (d, ${}^{2}J_{P-P} = 18$ Hz, P2)	
19	-4221.5 (t, ${}^{1}J_{Pt-P} = 2863$ Hz)	19.84 (s)	

^a All spectra were recorded in CD_2Cl_2 except for spectra of complexes 9, 11, and 13 which were measured in C_6D_6 .

inum complex of TCNE and presumably, although not identified, free cycloheptyne and cyclohexyne.⁵ It occurred to us that it might be possible to release dibenzotropynone from 5 in the same way. Indeed, treatment of a C_6D_6 solution of 5 with 1 equiv of TCNE led to a rapid change in color from yellow to dark redbrown. The ¹H NMR spectrum of the crude reaction mixture showed complete loss of 5. Workup gave the TCNE adduct of bis(triphenylphosphine)platinum (essentially quantitatively) and a 45% yield of a hydrocarbon that showed spectra consistent with a very interesting substituted benzene 14, a formal trimer of dibenzotropynone (Scheme 3). This structure was confirmed by an X-ray crystal structure analysis.

Crystal Structure of Trimer 14. Crystals of 14 were grown by slow evaporation of a methylene chloride/ hexane solution at room temperature. The structure of 14 was solved in a triclinic space group $P\overline{1}$ using direct methods. Thermal ellipsoid and stereographic drawings of 14 are presented in Figures 3 and 4, respectively, while crystal data are listed in Table 5. Selected bond lengths and angles and final fractional atomic coordinates are provided in Tables 3 and 7, respectively. The structure shows three dibenzotropone fragments fused to the benzene ring located in the center of the molecule. To minimize nonbonding interactions between the large dibenzotropone fragments, two of them bend in opposite directions forming dihedral angles between phenyl rings in the two fragments of 112.3 and 115.9°, respectively. The third fragment with a dihedral angle between phenyl rings of 158.2° is positioned in a unique way with one phenyl ring above and the other below the middle benzene ring. The consequence of such a spatial arrangement of these three fragments is a substantial twisted boat deformation (Figure 2) of the benzene ring in the center of the molecule. This distortion is quite severe and is comparable to other previously reported distorted benzenes. For example, the dihedral angle between planes C10-C11-C40 and C26-C25-C41, 38.4(4)°, is equal, within experimental error, to the corresponding dihedral angle in 8,9-dicarbomethoxy-[6]-para-cyclophane⁹ (38.9°) but is less than the most highly distorted ring reported to date, perchlorotriphenylene,¹⁰ which has a dihedral angle of 54.1°. Other more severely distorted benzenes



Figure 2.



Figure 3. Structure and labeling scheme for 14 with 40% probability of thermal ellipsoids.

include tetramethyl-[6](9,10)anthracenophane¹¹ (49.3 $^{\circ}$ dihedral) and [6](1,4)anthracenophane¹² (42° dihedral). Theoretical work on deformed benzenes has also recently appeared.¹³ There is a slight bond alternation (0.03 Å) in the middle benzene ring of 14, presumably as a result of a distortion. In perchlorotriphenylene this value is larger (0.06 Å), which is consistent with more severe distortion in this molecule.¹⁴

The trimer 14 exhibits approximately C_2 geometry in the solid state. If this structure is maintained in solution, however, it must undergo a rapid conformational equilibrium because the ¹H NMR clearly shows only 4 different kinds of aromatic hydrogens (if 14 were not equilibrating it should show 12) and the ¹³C NMR

⁽⁹⁾ Krieger, C.; Liebe, J.; Tochtermann, W. T. Tetrahedron Lett. 1983, 24, 707.

⁽¹⁰⁾ Shibata, K.; Kulkarni, A. A.; Ho, D. M.; Pascal, R. A., Jr. J. Am. Chem. Soc. 1994, 116, 5983.

⁽¹¹⁾ Tobe, Y.; Ishii, H.; Saiki, S.; Kakiuchi, K.; Naemura, K. J. Am.

Chem. Soc. **1993**, *115*, 11604. (12) Bickelhaupt, F. Pure Appl. Chem. **1990**, 62, 373. (13) Tsuzuki, S.; Tanabe, K. J. Chem. Soc., Perkin Trans. 2, **1990**, 1687.



Figure 4. Stereoview of compound 14.



spectrum shows only 8 kinds of carbon while nonequilibrating 14 should show 23. Furthermore, if it has C_2 symmetry in solution, the inversion barrier must be quite low since the ¹H NMR spectrum at -80 °C (C_6D_5 - CD_3) showed no significant broadening.

Synthesis and Structure of Complex 15. To test the generality of the trimerization reaction other alkyne complexes were subjected to reaction with TCNE. Complex 11, when treated with TCNE in C₆D₆, gave trimer 14 in yields comparable to those of complex 5 together with two unidentified platinum products which were detected in the ${}^{31}P{}^{1}H{}$ NMR. When the same reaction was carried out with complex 10, a mixture of organic products containing only about 5–10% (by ¹H NMR) 14 was formed. [(Cy₂PCH₂)₂Pt(TCNE)] (13a) was formed quantitativaly in this reaction. The reason for this difference in behavior is not clear.

Treatment of **6** with TCNE (Scheme 3) led to an interesting product. In addition to 10% of the TCNE complex of bis(triphenylphosphine)platinum (${}^{31}P{}^{1}H{}$ NMR), **6** gave the coupling product **15** (55% yield isolated); this type of reaction is quite unusual for platinum alkyne complexes.¹⁵ The initial structural assignment to **15** was based on elemental analysis and multinuclear NMR. The ¹H NMR of this material

⁽¹⁴⁾ For other examples of benzene rings with significant bond alternation see: Boese, R.; Blaser, D.; Billups, E. W.; Haley, M. M.; Maulitz, A. H.; Mohler, D. L.; Vollhardt, K. P. C. Angew. Chem., Int. Ed. Engl. **1994**, 33, 313. and references therein.

⁽¹⁵⁾ Moseley, K.; Maitlis, M. P. J. Chem. Soc., Dalton Trans. 1974, 169.



Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 14

		_		
Bond Lengths (Å)				
C11-C10	1.404(5)	C30-C20	1.491(5)	
C26-C10	1.433(4)	C27 - C25	1.487(3)	
C26-C25	1.398(4)	C29-C26	1.489(5)	
C41 - C25	1.424(5)	C43-C35	1.488(3)	
C41-C40	1.394(4)	C42-C40	1.490(5)	
C40-C11	1.430(5)	C44-C41	1.494(5)	
C14 - C11	1.490(5)	C12-C13	1.405(4)	
C12-C10	1.488(4)	C14-C15	1.418(5)	
C5 - O1	1.224(5)	C27 - C28	1.397(5)	
C20-O2	1.210(5)	C29-C30	1.404(5)	
C35 - O3	1.214(4)	C42-C43	1.402(5)	
C13-C5	1.482(6)	C44-C45	1.403(5)	
C28 - C20	1.492(5)			
	Bond An	gles (deg)		
C25-C41-C40	119.0(3)	C28-C20-C30	114.3(3)	
C26-C10-C11	117.6(3)	C30-C20-O2	122.7(3)	
C41-C40-C11	119.5(3)	C27-C25-C41	118.5(3)	
C41-C25-C26	118.4(2)	C29-C26-C10	117.2(3)	
C10-C26-C25	119.1(3)	C43-C35-C45	113.8(3)	
C40-C11-C10	116.3(3)	C42 - C40 - C11	118.1(3)	
C14-C11-C40	120.6(3)	C44-C41-C40	123.4(3)	
C12-C10-C26	119.9(3)	C43-C35-O3	122.3(3)	
C13-C5-C15	124.5(3)	C45 - C35 - O3	123.2(3)	
C13-C5-O1	116.9(4)	C28-C20-O2	122.1(3)	
C15-C5-O1	118.6(4)	C41-C40-C42	121.7(3)	
C29-C26-C25	123.4(2)	C26 - C25 - C27	123.1(3)	
C28-C20-C30	114.3(3)	C11-C10-C12	121.2(2)	

showed eight different protons belonging to the ligand. In the ${}^{31}P{}^{1}H$ NMR, two phosphorus nuclei (P1 and P2) were observed as nonequivalent doublets at 13.7 and 14.6 ppm, respectively (${}^{2}J_{P1-P2} = 20.5 \text{ Hz}$). The ${}^{195}\text{Pt}$ -{¹H} NMR exhibited a doublet of doublets centered at -4347.3 ppm with two different coupling constants to P1 (${}^{1}J_{Pt-P1} = 3259.4 \text{ Hz}$) and P2 (${}^{1}J_{Pt-P2} = 1918.2 \text{ Hz}$). This difference in coupling constants is presumably due to a stronger trans influence on P2 than on P1.

Crystals of complex 15 were obtained by slow evaporation of a methylene chloride/hexane solution. Complex 15 crystallizes in monoclinic space group Ia together with one molecule of methylene chloride solvent. The thermal ellipsoid drawing of the structure is shown in Figure 5, while crystal data are listed in Table 5.



X = 0

15



Figure 5. Structure and labeling scheme for 15 with 40% probability of thermal ellipsoids.

Selected bond lengths and angles and final fractional atomic coordinates are provided in Tables 4 and 8, respectively. Complex 15 can be viewed as a platinacyclopent-2-ene with platinum bonded to two phosphorus and two carbon atoms. The Pt-P1 bond [2.305(3) Å] is shorter than Pt–P2 [2.370(3) Å] as expected from two different ¹⁹⁵Pt-³¹P coupling constants. Correlation between bond distances of Pt-P and ¹⁹⁵Pt-³¹P coupling constants is well established.¹⁶ The Pt-C9 bond [2.090(9) Å] is shorter than Pt-C16 [2.161(9) Å], a difference which is attributed to the different hybridization of the two carbons bonded to the platinum atom. From this data it is clear that C9 (sp^2) exerts a stronger trans influence than does C16 (sp^3) . The Pt-C9 and Pt-C16 bond lengths are equal within experimental error to the

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 15

		T			
Bond Lengths (Å)					
Pt-P1	2.305(3)	C18-N1	1.10(2)		
Pt-P2	2.370(3)	C17-N2	1.11(2)		
Pt-C9	2.090(9)	C19-N3	1.14(2)		
Pt-C16	2.161(9)	C20-N4	1.14(2)		
P1-C51	1.825(11)	C10-C9	1.327(14)		
P1-C61	1.833(12)	C13-C9	1.474(15)		
P1-C71	1.833(11)	C11-C10	1.475(14)		
P2-C21	1.796(11)	C16-C15	1.609(14)		
P2-C31	1.831(11)	C17-C15	1.51(2)		
P2-C41	1.828(11)	C18-C15	1.51(2)		
C12-O	1.375(14)	C19-C16	1.465(14)		
C14-O	1.42(2)	C20-C16	1.46(2)		
	Bond Angles (deg)				
P1-Pt-P2	97.50(11)	C16-C15-C18	108.7(8)		
P2-Pt -C16	93.2(3)	C16-C15 -C10	104.7(8)		
P2-Pt -C9	168.2(2)	C12-O-C14	108.5(9)		
P1-Pt-C16	165.0(3)	C17-C15-C18	106.6(9)		
C9-Pt-C16	77.0(3)	C17-C15-C10	109.2(8)		
Pt-C16-C15	98.7(6)	C18-C15-C10	118.6(8)		
C10-C9-Pt	117.0(7)	C19-C16-C20	108.2(9)		
C10-C9-C13	121.1(9)	C19-C16-Pt	121.7(7)		
C13-C9-Pt	121.4(7)	N2-C17-C15	177.4(12)		
C11-C10-C15	120.7(9)	N1-C18-C15	174.4(13)		
C11-C10-C9	127.4(9)	N3 -C19-C16	175.3(13)		
C16-C15-C17	108.7(8)	N4-C20-C16	178.0(14)		

corresponding bond distances observed in Pt(cyclohexenyl) $(CH_2COC_6H_5)(diphos)$ [Pt-C(sp²) = 2.068(10) Å, $Pt-C(sp^3) = 2.175(10)$ Å].¹⁷ Complex 15 has a distorted square planar geometry around the Pt atom with the dihedral angle between the planes defined by Pt, P1, P2 and Pt, C9, C16 equal to $12.5(3)^{\circ}$. The dihedral angle between the phenyl ring planes of the dibenzoxepin ligand [109.6(4)°] is much smaller than that of free dibenzoxepin¹⁸ [134(2)°]. The most pronounced feature of the structure of 15 is the presence of a platinacyclopent-2-ene ring which has a geometry of a half-chair. The atoms Pt, C9, C10, and C15 are coplanar (maximum deviation from the least squares plane is 0.016 Å for C10) while C16 lies 0.97 Å below the plane. The dihedral angle between the Pt-C9-C10-C15 and the Pt-C16-C15 plane is $54.7(6)^{\circ}$. Such distortions from planarity are a common feature of metallacyclopent-2-enes.¹⁹ This distortion, however, is significantly larger in 15 than in any other metallacyclopent-2-enes known for which crystal structure data are available.²⁰ It is not clear why 5 and 6 react differently with TCNE.

Preparation of Dibenzotropyne 16. The platinum complex of tropyne (1) was prepared by hydride abstraction from the corresponding cycloheptadienyne complex. The dibenzannelated anologue (7) behaved similarly. Treatment of 7 with triphenylcarbenium tetrafluoroborate in methylene chloride at -78 °C, followed by warming to room temperature, gave a deep blue solution. Addition of diethyl ether gave 16 as deep blue-

Am. Chem. Soc: 1973, 95, 3028.

(20) Cambridge Data Base.

black needles (Scheme 4). Complex 16 was characterized by ¹H, ¹³C, ¹⁹F, ³¹P, and ¹⁹⁵Pt NMR, HRMS, and elemental analysis. In the ¹H NMR all protons belonging to the ligand are deshielded relative to 7. The electronic structure of 16 is somewhat different from that of 1 in that the positive charge in 16 resides to a greater extent on the ligand. This is best shown by the ¹H and ¹⁹⁵Pt $\{^{1}H\}$ NMR. The chemical shift of H5 in **16** is the same (10.45 ppm) as that of the corresponding proton in the dibenzotropylium ion.²¹ However, the same proton in complex 1 (8.64 ppm) shows a significant upfield shift when compared to the tropylium ion (9.55 ppm).¹ Similarly, the chemical shift in the $^{195}Pt{^{1}H}$ NMR of 16 is 280 ppm upfield relative to 1. Both of these differences are expected if the platinum atom more effectively delocalizes the positive charge in 1 than in 16.

Reactivity of Platinum Tropyne Complex 16. Tropyne complexes of platinum have two reaction sites, one on the ring which is susceptible to nucleophilic attack and the other on the metal center where electrophilic attack would be expected. Examples of these two reaction types for 16 are shown in Scheme 4. Reaction with KBEt₃H is rapid and gives 7 in 70% yield (¹H and ³¹P{¹H} NMR). Three minor phosphoruscontaining platinum products were formed in this reaction as shown by ${}^{31}P{}^{1}H{}$ NMR, but they were not characterized. The bidentate phosphine bis(dicyclohexylphosphino)ethane also reacts rapidly (within seconds) with 16 to form the bis(alkyne) complex 17. The ³¹P{¹H} NMR of this material exhibits two peaks, one centered at 21.95 ppm (PPh₃, ¹⁹⁵Pt satellites) and the other at 34.93 ppm (PCy₂). The ratio of cyclohexyl to phenyl protons in the ¹H NMR is consistent with the stoichiometry of complex 17. This reaction parallels the reaction of metal η^7 -tropylium complexes with diphosphines.²² Addition of HBr in acetic acid to a THF solution of 16 led to a rapid color change from deep blue to purple. Addition of ether gave 18 as a purple precipitate. The ³¹P{¹H} NMR of 18 showed only two doublets with ¹⁹⁵Pt satellites corresponding to the *cis*isomer. Upon standing, this slowly isomerized to the trans-isomer (ca. 70% conversion within 4 weeks at room temperature in CD_2Cl_2). The same type of products was obtained from reaction of 1 with HBr and HCl.¹

Experimental Section

General Considerations. All experiments involving organometallic compounds were carried out under an atmosphere of purified N₂ using Schlenk, vacuum line, and drybox techniques. Solvents were distilled under nitrogen prior to use: toluene, THF, and Et₂O from sodium benzophenone ketyl; hexane from sodium benzophenone ketyl/tetraglyme mixture; methylene chloride from CaH₂. NMR spectra were measured on a Varian XL-300 (FT 300 MHz, ¹H; 75 MHz, ¹³C; 282 MHz, ¹⁹F; 121 MHz, ³¹P; 64 MHz, ¹⁹⁵Pt). ¹H NMR and ¹³C{¹H} NMR spectra were referenced to residual solvent peaks and are reported in ppm relative to tetramethylsilane. ¹⁹F NMR spectra were referenced to external $CFCl_3$. ${}^{31}P{}^{1}H} NMR$ spectra were referenced to external 85% H₃PO₄ in D₂O. ¹⁹⁵Pt-¹H} NMR spectra were referenced to an external saturated solution of Na₂PtCl₆ in D₂O. Infrared spectra were measured in KBr pellets on a Perkin-Elmer 1600 FTIR spectrometer.

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Scheme 4



Mass spectra (positive FAB) were obtained on a Finnigan Mat 95Q. Elemental analyses were performed in the microanalysis lab in the Chemistry Department at the University of Florida. Melting points were measured in open capillaries and are not corrected. Potassium *tert*-butoxide, tetrafluoroboric acid, hydrogen bromide (30 wt % solution in acetic acid), potassium triethylborohydride (1.0 M solution in THF), tetracyanoethylene, *tert*-butyl isocyanide, and triphenylcarbenium tetrafluoroborate were purchased from Aldrich Chemical Co., and 1,2bis(dicyclohexylphosphino)ethane was purchased from Strem Chemicals. All compounds were used as received. The following compounds were prepared as described in the literature without any modification: $Pt(PPh_{3})_{3}$,²³ 10-bromodibenzosuberone,²⁴ 10,11-dibromodibenzooxepin,²⁵ 10,11-dibromodibenzocycloheptene.²⁶

(10,11-Didehydrodibenzotropone)bis(triphenylphosphine)platinum C₆H₃CH₃ (5). Pt(PPh₃)₃ (0.3 g, 0.306 mmol) and K-O^tBu (0.068 g, 0.612 mmol) were disolved in 10 mL of THF. To this solution was added very slowly 10bromodibenzosuberone (0.142 g, 0.5 mmol) in 2 mL of THF at room temperature. After stirring of the mixture for 1 h, the solvent was evaporated and the residue was extracted with 5-10 mL of toluene. To this mixture was added 3 mL of hexane, and the yellow solution was filtered. To the filtrate was added 30 mL of hexane, and the Schlenk tube was put aside in the refrigerator for 4 days to give 200 mg yellow crystals (65%). The compound crystallizes as a toluene solvate. Mp: 225 °C dec. IR (KBr): 1708, 1622, 1585.8, 1479, 1434.6, 1303.9, 1092.6, 754.4, 695.7 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 8.22 (d, 2H, ³J_{H4-H3} = 7.9 Hz, H4), 7.62 (m, 12H, PPh₃, ortho), 7.26 (m, 25H), 7.02 (td, 2H, ${}^{3}J_{H2-H1,3} = 7.9$ Hz, ${}^{4}J_{H2-H4} = 1.44$ Hz, H2), 6.43 (d, 2H, ${}^{3}J_{H1-H2} = 7.9$ Hz, H1). ${}^{13}C{}^{1}H{}$ NMR (CD₂-Cl₂): δ 195.66, 140.33 (t, $J_{C-P} = 3.56$ Hz, $J_{C-Pt} = 44.01$ Hz), 136.39 (vd, ${}^{1}J_{C-P} = 49.34$ Hz, PPh₃, ipso), 134.56 (m, PPh₃, ortho), 132.43 (dd, ${}^{2}J_{C-Pcis} = 8.23$ Hz, ${}^{2}J_{C-Ptrans} = 84.56$ Hz), 131.55, 130.86, 130.69 (t, 20.7 Hz), 130.41, 129.92 (s, PPh₃, para), 128.44 (t, ${}^{3}J_{C-P} = 4.62$ Hz, PPh₃, meta), 127.01. HRMS (FAB) (m/e): calcd for (M + 1)⁺, 924.2124, found, 924.2114. Anal. Calcd for C₅₈H₄₆OP₂Pt: C, 68.54; H, 4.56. Found: C, 68.54; H, 4.65.

(10,11-Didehydrodibenzooxepin)bis(triphenylphosphine)platinum (6). $Pt(PPh_3)_3$ (0.5 g, 0.51 mmol) and K-O'Bu (0.252 g, 0.2.25 mmol) were dissolved in 15 mL of THF. To this solution was added very slowly 10,11-dibromodibenzooxepin (0.318 g, 0.9 mmol) in 3 mL of THF at room temperature. After stirring of the mixture for 4 h, the solvent was evaporated and the residue was extracted with 20 mL of toluene and 30 mL of hexane was added causing quick precipitation of 17 containing 15% of starting material. This solid was recrystallized from a mixture of toluene and hexane to give 286 mg of analytically pure yellow crystals (61.6%). Mp: 223-225 °C dec. IR (KBr): 3052.2 w, 1691.5, 1586.6 w, 1478.4, 1434.9, 1195.1, 1094, 777, 742.8, 693.6, 536,8, 519.3 cm $^{-1}.~^1H$ NMR (CD₂Cl₂): δ 7.48 (m, 12H, PPh_3, ortho), 7.2 (m, 18H, PP h_3), 7.05 (td, 2H, ${}^{3}J_{H3-H4,2} = 7.6$ Hz, ${}^{4}J_{H3-H1} = 1.6$ Hz, H3), 6.54 (td, 2H, ${}^{3}J_{H2-H3,1} = 7.4$ Hz, ${}^{4}J_{H2-H4} = 1.5$ Hz, H2), 6.43 (dd, 2H, ${}^{3}J_{\text{H1-H2}} = 7.6 \text{ Hz}$, ${}^{4}J_{\text{H1-H3}} = 1.4 \text{ Hz}$, H1). ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR (CD₂Cl₂): δ 155.2 (t, $J_{C-P} = 2.7$ Hz, $J_{C-Pt} = 37.94$ Hz), 136.64 (vd, ${}^{1}J_{C-P} = 46.79$ Hz, PPh₃, ipso), 134.43 (${}^{2}J_{C-P} = 6.5$ Hz, PPh₃, ortho), 133.39 (dd, ${}^{2}J_{C-Pcis} = 8.01$ Hz, ${}^{2}J_{C-Ptrans} = 86.9$ Hz), 129.78 (s, PPh₃, para), 128.59, 128.44, 128.27 (t, ${}^{3}J_{P-C} =$ 4.6 Hz, PPh₃, meta), 127.44 (t, 10.35 Hz), 124.8, 121.16. HRMS (FAB) (m/e): calcd for $(M + 1)^+$, 912.2124; found, 912.2103. Anal. Calcd for C₅₀H₃₈OP₂Pt: C, 65.86; H, 4.2. Found: C, 66.05; H, 4.21.

(10, 11-Dide hydrodiben zocycloheptene) bis (triphen-

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Table 5. Crystallographic Data					
	5	14	15		
	A. Crystal Data (2	98 K)			
$a, \mathrm{\AA}$	11.221(2)	11.274(2)	17.175(3)		
<i>b</i> , Å	14.318(2)	11.826(1)	15.411(2)		
c, A	16.621(4)	13.474(2)	18.661(2)		
α, deg	74.22(2)	111.79(1)	90		
β , deg	78.86(2)	106.34(1)	91.86(1)		
γ , deg	73.56(2)	98.54(1)	90		
$V, Å^3$	2445.0(9)	1534.9(4)	4937(1)		
$d_{ m calc},{ m g}~{ m cm}^{-3}(298~{ m K})$	1.380	1.326	1.520		
empirical formula	$\mathrm{C}_{51}\mathrm{H}_{38}\mathrm{OP}_{2}\mathrm{Pt}\cdot\mathrm{C}_{7}\mathrm{H}_{8}$	$C_{45}H_{24}O_3$	$C_{56}H_{38}N_4OP_2Pt$ · CH_2Cl_2		
fw	1015.98	612.64	1124.86		
cryst system	triclinic	triclinic	monoclinic		
space group	$P\overline{1}$	$P\bar{1}$	Ia		
Ζ	2	2	4		
F(000), electrons	1020	636	2240		
cryst size, mm ³	0.63 imes 0.30 imes 0.06	0.42 imes 0.38 imes 0.34	$0.61 \times 0.19 \times 0.11$		
	B. Data Collection ((298 K)			
radiation (λ, \dot{A})		Μο Κα (0.710 73)			
mode		w-scan			
scan range	symm	etrically over 1.2° about $K_{\alpha 1}$	maximum		
background	offset	1.0 and -1.0 in ω from K _{01.2}	maximum		
scan rate, deg min ^{-1}	4-8	3-6	3-6		
2θ range, deg	3-55	3-50	3-58		
range of <i>hkl</i>	$0 \le h \le 13$	$0 \le h \le 14$	$0 \le h \le 24$		
5	$-16 \le k \le 16$	$-15 \le k \le 15$	$0 \le k \le 22$		
	$-19 \leq l \leq 19$	$-17 \leq l \leq 17$	$-26 \le l \le 26$		
tot, reflcns measd	9103	5695	6853		
unique reflcns	8619	5394	6625		
abs coeff μ (Mo K α), mm ⁻¹	2.97	0.08	3.07		
	C. Structure Refinement				
S. goodness-of-fit	1.8940	1.6522	1.4121		
reflcns used	6230, $I > 3\sigma(I)$	$3722, I > 2\sigma(I)$	5569, $I > 2\sigma(I)$		
no. of variables	554	529	587		
$R, \mathbf{w} R^{a} (\%)$	5.79, 6.75	6.17, 6.13	4.74, 4.76		
$R_{\rm int.} \%$	0.000	0.0352	0.000		
max shift/esd	0.009	0.001	0.002		
min peak in diff Fourier map, e Å ⁻³	-1.9	-0.2	-1.6		
max peak in diff Fourier map, e Å ⁻³	1.2	0.3	1.8		
······································		-			

^{*a*} Relevant expressions are as follows, where in the footnote F_o and F_c represent, respectively, the observed and calculated structure-factor amplitudes. Function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$. $R = \sum (||F_o| - |F_c||)/\sum |F_o|$; $wR = [\sum w(|F_o| - |F_c|)^2/\sum |F_o|^2]^{1/2}$; $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

ylphosphine)platinum (7). To a solution of $Pt(PPh_3)_3$ (0.45) g, 0.458 mmol) and K-O^tBu (228 mg, 2 mmol) in 15 mL of THF was added very slowly (1 h) 10,11-dibromodibenzocycloheptene (285 mg, 0.81 mmol) in 3 mL of THF at room temperature. After stirring of the mixture for 2 h, the solvent was removed and the residue was extracted with 5-10 mL of toluene. To this filtrate was added hexane, and the Schlenk tube was cooled to -26 °C to give 280 mg (67%) of 7 as an off-white solid. An analytically pure sample was obtained by recrystallization from a mixture of toluene and hexane. Mp: 219-222 °C dec. IR (KBr): 3051.2 w, 1688.7, 1586.7 w, 1477.8, 1434.3, 1092.8, 751.5, 693.2, 540.1, 519, 496.8 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 7.5 (m, 12H, PPh₃), 7.31 (d, 2H, ³J_{H4-H3} = 7.3 Hz, H4), 7.23 (m, 18H, PPh₃), 7.08 (td, 2H, ${}^{3}J_{H3-H4,2} = 7.4$ Hz, $_{4}J_{\text{H3}-\text{H1}} = 1.3 \text{ Hz}, \text{H3}), 6.65 \text{ (td, 2H, } {}^{3}J_{\text{H2}-\text{H3},1} = 7.5 \text{ Hz}, {}^{4}J_{\text{H2}-\text{H4}}$ = 1.2 Hz, H2), 6.43 (dd , 2H, ${}^{3}J_{H1-H2}$ = 7.6 Hz, ${}^{4}J_{H1-H3}$ = 1.2 Hz, H1), 3.85 (s, 2H, CH₂). ${}^{13}C{}^{1}H$ NMR (CD₂Cl₂): δ 134.4 (m), 134.65 (m, PPh₃), 132.62 (t, $J_{C-P} = 9.5$ Hz), 129.78 (s, PPh_3), 128.53, 128.31 (m, PPh_3), 127.52 (s, $J_{C-Pt} = 25.35 \text{ Hz}$), 126.92, 126.27, 44.08. HRMS (FAB) (m/e): calcd for (M + 1)⁺, 910.2332; found, 910.2323. Anal. Calcd for C_{51} -H₄₀P₂Pt: C, 67.32; H, 4.43. Found: C, 67.36; H, 4.55.

Preparation of Complex 8. To a Schlenk tube containing 120 mg of **5** (0.12 mmol) in 10 mL of CH₂Cl₂, 22.5 mg of HBF₄ (0.118 mmol) in 2 mL of CH₂Cl₂ was added slowly at -78 °C. After slow warming of the solution to room temperature, hexane was added and the Schlenk tube was placed in a refrigerator for a few days. Solvent removal gave 105 mg of **8** (86%). IR (KBr): 3050 w, 1637, 1596, 1572, 1482, 1437, 1313, 1098, 745, 693, 523 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 9.0 (dd, 1H, ${}^{3}J_{H-H} = 7.8$ Hz, ${}^{4}J_{H-H} = 1$ Hz), 7.77 (dd, 1H, ${}^{3}J_{H-H} = 7.1$ Hz, ${}^{4}J_{H-H} = 2.1$ Hz), 7.56 (dd, 1H, ${}^{3}J_{H-H} = 7.8$ Hz, ${}^{4}J_{H-H} = 1.5$ Hz),

 $\begin{array}{l} 7.2-7.5 \ (\mathrm{m},\ 33\mathrm{H},\ PPh_3)\ 7.15 \ (\mathrm{td},\ 1\mathrm{H},\ ^3J_{\mathrm{H-H}}=7.3 \ \mathrm{Hz},\ ^4J_{\mathrm{H,H}}=1.2 \ \mathrm{Hz}),\ 7.03 \ (\mathrm{s},\ 1\mathrm{H},\ ^3J_{\mathrm{H-Pt}}=99.7 \ \mathrm{Hz}),\ 6.43 \ (\mathrm{dd},\ 1\mathrm{H},\ ^3J_{\mathrm{H-H}}=7.1 \ \mathrm{Hz},\ ^4J_{\mathrm{H-H}}=1.9 \ \mathrm{Hz}),\ 3.73 \ (\mathrm{s},\ \mathrm{br}).\ ^{13}\mathrm{C}\{^{1}\mathrm{H}\}\ \mathrm{NMR}\ (\mathrm{CD}_2\mathrm{Cl}_2): \\ \delta\ 193.08,\ 139.3,\ 138.19 \ (\mathrm{s},\ \mathrm{br}),\ 137.49,\ 136.52,\ 135.7,\ 135.55,\ 134.37 \ (\mathrm{t},\ ^2J_{\mathrm{C-P}}=6.2\mathrm{Hz},\ PPh_3,\ \mathrm{ortho}),\ 131.98 \ (\mathrm{s},\ PPh_3,\ \mathrm{para}),\ 131.42,\ 130.65,\ 129.7,\ 129.39 \ (\mathrm{t},\ ^3J_{\mathrm{C-P}}=5.45 \ \mathrm{Hz},\ PPh_3,\ \mathrm{meta}),\ 128.91,\ 127.94,\ 127.42,\ 127.09,\ 127.05,\ 126.67.\ ^{19}\mathrm{F}\ \mathrm{NMR}\ (\mathrm{CD}_2-\mathrm{Cl}_2): \\ \delta\ -150.58.\ \mathrm{HRMS}\ (\mathrm{FAB})\ (m/e):\ \mathrm{calcd}\ \mathrm{for}\ (\mathrm{M}-\mathrm{H}_2\mathrm{O})^+,\ 925.2203;\ \mathrm{found},\ 925.2283.\ \mathrm{Anal.}\ \mathrm{Calcd}\ \mathrm{for}\ \mathrm{C}_{52}\mathrm{H}_{44}-\mathrm{Cl}_2\mathrm{BF}_4\mathrm{O}_2\mathrm{P}_2\mathrm{Pt}:\ \mathrm{C},\ 56.00;\ \mathrm{H},\ 3.97.\ \mathrm{Found}:\ \mathrm{C},\ 55.82;\ \mathrm{H},\ 3.96. \end{array}$

(10,11-Didehydrodibenzooxepin)[bis(dicyclohexylphosphino)ethane]platinum (9). A 100 mg (0.108 mmol) amount of 6 and 50 mg (0.118 mmol) of bis(dicyclohexylphosphino)ethane were dissolved in 0.5 mL of $C_6 D_6$ in an NMR tube. After 4 days at room temperature the ${}^{31}P{}^{1}H$ NMR showed formation of complex 9 in about 95% yield. The solution from the NMR tube was transferred to a Schlenk tube, and 4 mL of hexane was added. After 1 week at 6 °C yellow crystals had formed: 45 mg (yield 50.6%); mp 248-250 °C dec. IR (KBr): 2926, 2848, 1674, 1469, 1438, 1193, 742 cm⁻¹. 1 H NMR (C₆D₆): δ 7.68 (dd, 2H, ${}^{3}J_{H-H} = 7.4 \text{ Hz}, {}^{4}J_{H-H} = 1.7 \text{ Hz}),$ 7.29 (d, 2H, ${}^{3}J_{H-H} = 7.9$ Hz), 7.15 (td, 2H, ${}^{3}J_{H-H} = 7.4$ Hz, ${}^{4}J_{H-H}$ = 1.4 Hz,), 7.06 (td, 2H, ${}^{3}J_{H-H}$ = 7.8, ${}^{4}J_{H-H}$ = 1.7 Hz), 2.19 (d, 4H, J = 11.8 Hz), 0.95–2 (m, 44H, PCy₃). ¹³C{¹H} NMR (C₆D₆): δ 156.2 (t, $J_{C-P} = 2.7$ Hz), 144.23 (dd, ${}^{2}J_{C-Pcis} = 13.46$ Hz, ${}^{2}J_{C-Ptrans} = 99.6$ Hz), 131.51 (t, $J_{C-P} = 11.3$ Hz), 129.07, $128.12,\ 124.93,\ 121.89,\ 36.35\ (m),\ 30.33,\ 29.22,\ 27.25\ (m),$ 26.38, 24.8 (m). HRMS (FAB) (m/e): calcd for $(M + 1)^+$, 810.3533; found, 810.3428. Anal. Calcd for C₄₀H₅₆OP₂Pt: C, 59.30; H. 6.97. Found: C, 59.15; H, 7.01.

(10,11-Didehydrodibenzotropone)[bis(dicyclohexylphosphino)ethane]platinum (10). A 130 mg (0.13

Table 6. Fractional Coordinates and Equivalent Isotropic^a Thermal Parameters (Å²) for the Non-H Atoms of Complex 5

atom	x	у	z	U
Pt	0.96571(4)	0.15781(3)	0.77442(3)	0.0350(2)
P 1	1.1114(3)	0.0522(2)	0.7019(2)	0.0368(11)
P2	0.7913(3)	0.1002(2)	0.7891(2)	0.0369(11)
0	0.9708(11)	0.5478(7)	0.8214(9)	0.115(7)
C1	1.2663(11)	0.2716(10)	0.7399(8)	0.059(6)
C2	1.3582(13)	0.3241(10)	0.7190(10)	0.074(7)
C3	1.327(2)	0.4162(13)	0.7383(11)	0.096(9)
C4	1.2092(14)	0.4579(10)	0.7770(10)	0.074(7)
C5	0.9989(15)	0.4528(10)	0.8409(10)	0.073(7)
C6	0.852(2)	0.4509(12)	0.9753(12)	0.095(9)
C7	0.771(2)	0.408(2)	1.0386(11)	0.113(12)
C8	0.746(2)	0.324(2)	1.0346(11)	0.098(10)
C9	0.7991(11)	0.2806(11)	0.9704(8)	0.062(6)
C10	0.9408(11)	0.2663(8)	0.8399(7)	0.044(5)
C11	1.0467(10)	0.2592(8)	0.7930(6)	0.038(4)
C12	1.1435(11)	0.3111(9)	0.7782(7)	0.051(5)
C13	1.1184(13)	0.4039(9)	0.7986(9)	0.060(6)
C14	0.8795(11)	0.3157(8)	0.9057(7)	0.048(5)
C15	0.9119(13)	0.4059(11)	0.9050(9)	0.068(7)
C21	0.8101(10)	-0.0325(8)	0.8436(7)	0.044(5)
C22	0.7826(11)	-0.1028(9)	0.8115(8)	0.055(5)
C23	0.8091(12)	-0.2025(9)	0.8593(10)	0.063(6)
C24	0.8530(15)	-0.2285(12)	0.9294(12)	0.083(8)
C25	0.8786(13)	-0.1596(13)	0.9624(9)	0.081(7)
C26	0.8591(11)	-0.0585(9)	0.9185(8)	0.057(5)
C31	0.7221(10)	0.1206(8)	0.6924(7)	0.042(5)
C32	0.6083(10)	0.1030(9)	0.6928(8)	0.051(5)
C33	0.5538(12)	0.1251(10)	0.6189(8)	0.058(6)
C34	0.6106(13)	0.1683(10)	0.5451(9)	0.064(7)
C35	0.7277(15)	0.1882(11)	0.5411(8)	0.073(7)
C36	0.7832(11)	0.1637(10)	0.6149(7)	0.057(6)
C41	0.6513(10)	0.1629(8)	0.8486(7)	0.044(5)
C42	0.5629(11)	0.1139(11)	0.8984(7)	0.057(6)
C43	0.4552(12)	0.1679(11)	0.9376(8)	0.063(6)
C44	0.4355(12)	0.2671(12)	0.9317(9)	0.071(7)
C45	0.5217(13)	0.3165(11)	0.8818(9)	0.069(7)
C46	0.6296(12)	0.2641(10)	0.8408(8)	0.060(6)
C51	1.2474(10)	-0.0063(8)	0.7604(7)	0.040(5)
C52	1.2372(12)	-0.0010(9)	0.8436(7)	0.055(5)
C53	1.3351(12)	-0.0505(10)	0.8909(8)	0.063(6)
C54	1.4476(12)	-0.1024(9)	0.8543(8)	0.060(6)
C55	1.4591(11)	-0.1099(10)	0.7717(8)	0.061(6)
C56	1.3580(12)	-0.0608(10)	0.7252(8)	0.060(6)
C61	1.1794(10)	0.1096(8)	0.5976(7)	0.040(5)
C62	1.2556(11)	0.0520(9)	0.5395(7)	0.055(5)
C63	1.3134(12)	0.0995(10)	0.4646(7)	0.060(6)
C64	1.2979(12)	0.2022(11)	0.4454(8)	0.063(6)
C65	1.2257(13)	0.2567(10)	0.4999(8)	0.065(6)
055	1.1656(11)	0.2072(9)	0.5772(7)	0.054(6)
071	1.0786(10)	-0.0615(7)	0.6885(6)	0.036(4)
U72	1.1043(10)	-0.1497(9)	0.7479(7)	0.048(5)
073	1.0752(12)	-0.2333(9)	0.7379(9)	0.060(6)
074	1.0188(13)	-0.2288(11)	0.6715(9)	0.070(7)
075	0.9888(13)	-0.1404(11)	0.6109(8)	0.068(7)
076	1.0217(13)	-0.0577(10)	0.6196(7)	0.060(6)

^{*a*} For anisotropic atoms, the *U* value is U_{eq} , calculated as $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$, where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

mmol) amount of 5 and 60 mg (0.14 mmol) of bis(dicyclohexylphosphino)ethane were dissolved in 3 mL of C_6H_6 in a Schlenk tube, and the mixture was stirred for 20 h at room temperature. A 10 mL volume of hexane was added, and the solution was filtered through a canula. The filtrate was cooled for 1 week at -20 °C to give 80 mg of crystaline pure 10 (74%), mp 265 °C dec. IR (KBr): 2928, 2850, 1707, 1615, 1578, 1447, 1302, 751 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 8.25 (dd, 2H, ³J_{H4-H3} = 8.07 Hz, ${}^{4}J_{H4-H2} = 1.4$ Hz, H4), 7.81 (dd, 2H, ${}^{3}J_{H1-H2} = 7.8$ Hz, ${}^{4}J_{\text{H1}-\text{H3}} = 1.2 \text{ Hz}, \text{H1}$, 7.68 (td, 2H, ${}^{3}J_{\text{H3}-\text{H2},4} = 7.14 \text{ Hz}, {}^{4}J_{\text{H3}-\text{H1}}$ = 1.5 Hz, H3), 7.06 (td, 2H, ${}^{3}J_{H2-H1,3}$ = 7.55, ${}^{4}J_{H2-H4}$ = 1.4 Hz, H2), 1–2.2 (m, 44H, PCy₃). ${}^{13}C{}^{1}H}$ NMR (CD₂Cl₂): δ 195.8, 144.2 (dd, ${}^{2}J_{C-Pcis} = 14.3 \text{ Hz}$, ${}^{2}J_{C-Ptrans} = 97.3 \text{ Hz} 140.7$ (t, J_{C-P} = 3.8 Hz), 133.27 (t, J_{C-P} = 10.6 Hz), 132.18 (m), 131.14, 128.76, 126.9, 36.8 (m), 30.8 (s, $J_{C-Pt} = 23.5 \text{ Hz}$), 29.5 (s, J_{C-Pt} = 21 Hz), 27.54 (m) 26.7, 25 (t, J_{C-P} = 20.5 Hz). HRMS (FAB)

Table 7. Fractional Coordinates and EquivalentIsotropic^a Thermal Parameters (Å²) for the Non-HAtoms of Compound 14

		mo or comp	Jouna II	
atom	x	У	z	U
01	0.2157(3)	1.0224(2)	0.9121(3)	0.081(2)
O2	0.4222(2)	0.4639(2)	0.3601(2)	0.0566(13)
O3	0.0782(2)	0.1800(2)	0.7596(2)	0.0608(13)
C1	0.0944(3)	0.6117(4)	0.8857(3)	0.049(2)
C2	0.0243(4)	0.6545(4)	0.9527(4)	0.062(2)
C3	0.0350(4)	0.7828(4)	1.0024(4)	0.069(2)
C4	0.1080(4)	0.8625(4)	0.9770(3)	0.058(2)
C5	0.2442(3)	0.9222(3)	0.8849(3)	0.047(2)
C6	0.4407(4)	1.0271(3)	0.8750(3)	0.051(2)
C7	0.5397(4)	1.0346(3)	0.8370(3)	0.056(2)
C8	0.5477(4)	0.9259(3)	0.7552(3)	0.054(2)
C9	0.4565(3)	0.8129(3)	0.7144(3)	0.044(2)
C10	0.2733(3)	0.6695(3)	0.7099(3)	0.0329(14)
C11	0.2420(3)	0.6256(3)	0.7854(2)	0.0324(13)
C12	0.3528(3)	0.8019(3)	0.7520(3)	0.0355(14)
C13	0.3466(3)	0.9131(3)	0.8357(3)	0.039(2)
C14	0.1790(3)	0.6916(3)	0.8644(2)	0.0356(14)
C15	0.1782(3)	0.8205(3)	0.9063(3)	0.042(2)
C16	0.1636(3)	0.7111(3)	0.5071(3)	0.043(2)
C17	0.1440(4)	0.7583(3)	0.4266(3)	0.053(2)
C18	0.1919(4)	0.7172(3)	0.3400(3)	0.057(2)
C19	0.2574(4)	0.6271(3)	0.3341(3)	0.051(2)
C20	0.3287(3)	0.4647(3)	0.3874(3)	0.039(2)
C21	0.2094(4)	0.2387(3)	0.2727(3)	0.052(2)
C22	0.1237(4)	0.1294(4)	0.2518(3)	0.067(2)
C23	0.0729(4)	0.1258(3)	0.3317(3)	0.054(2)
C24	0.1090(3)	0.2310(3)	0.4345(3)	0.039(2)
C25	0.2389(3)	0.4501(3)	0.5768(2)	0.0304(13)
C26	0.2511(3)	0.5768(3)	0.5967(2)	0.0317(14)
C27	0.1958(3)	0.3441(3)	0.4599(2)	0.0318(13)
C28	0.2445(3)	0.3472(3)	0.3761(3)	0.0358(14)
C29	0.2297(3)	0.6197(3)	0.5039(3)	0.0343(14)
C30	0.2747(3)	0.5754(3)	0.4133(3)	0.0382(15)
C31	0.3857(3)	0.2678(3)	0.6002(3)	0.039(2)
C32	0.4104(4)	0.1505(3)	0.5729(3)	0.053(2)
C33	0.3494(4)	0.0635(3)	0.6005(3)	0.060(2)
C34	0.2689(4)	0.0951(3)	0.6599(3)	0.053(2)
C35	0.1780(3)	0.2493(3)	0.7729(3)	0.040(2)
C36	0.2834(3)	0.3550(4)	0.9834(3)	0.047(2)
C37	0.3600(4)	0.4564(4)	1.0860(3)	0.052(2)
C38	0.4052(3)	0.5728(4)	1.0873(3)	0.048(2)
C39	0.3733(3)	0.5861(3)	0.9865(3)	0.040(2)
C40	0.2619(3)	0.5058(3)	0.7752(2)	0.0321(14)
C41	0.2673(3)	0.4212(3)	0.6730(2)	0.0296(13)
C42	0.2960(3)	0.4840(3)	0.8804(2)	0.0334(14)
C43	0.2516(3)	0.3670(3)	0.8807(3)	0.0366(15)
C44	0.3031(3)	0.3010(3)	0.6589(2)	0.0328(13)
C45	0.2480(3)	0.2142(3)	0.6928(3)	0.0376(14)

^{*a*} For anisotropic atoms, the *U* value is U_{eq} , calculated as $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$, where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

(m/e): calcd for $(M+1)^+,\,822.3533;$ found, 822.3559. Anal. Calcd for $C_{41}H_{56}OP_2Pt:$ C, 59.91; H, 6.94. Found: C, 60.34; H, 6.93.

(10,11-Didehydrodibenzotropone)(triphenylphosphine)(tert-butyl isocyanide)platinum (11). To a Schlenk tube containing 100 mg of 5 (0.1 mmol) in 2 mL of C_6H_6 , was added 22 mg of *tert*-butyl isocyanide (0.26 mmol) in 30 mL of C_6H_6 . After the solution was stirred for 20 min at room temperature, the solvent was evaporated and the residue was dissolved in 1 mL of C_6H_6 followed by addition of 6 mL of hexane. After 2 days at 6 °C yellow-orange needles had formed: 63 mg (84%); mp 210 °C dec. IR (KBr): 3054 w, 2982 w, 2156, 1711, 1618, 1583 1436, 1304, 1206, 1096, 754, 696, 531, 518 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 8.35 (d, 1H, ³J_{H-H} = 7.8 Hz), 8.28 (d, 1H, ${}^{3}J_{H-H} = 7.7$ Hz), 7.87 (d, 1H, ${}^{3}J_{H-H} = 7.1$ Hz), 7.74 (m, 7H, PPh₃), 7.53 (t, 1H, ${}^{3}J_{H-H} = 7$ Hz), 7.43 (m, 9H, PPh₃), 7.35 (t, 1H, ${}^{3}J_{H-H} = 8.1$ Hz), 7.15 (t, 1H, ${}^{3}J_{H-H} = 7.5$ Hz), 6.81 (d, 1H, ${}^{3}J_{H-H} = 7.8$ Hz), 1.39 (s, 9H). ${}^{13}C{}^{1}H$ NMR (CD₂Cl₂): δ 194.73, 140.99 (s, J_{Pt-C} = 44.6 Hz), 139.97 (s, J_{P-C} = 8 Hz), 138.03, 136.53, 136.17 (d, J_{C-P} = 44.8 Hz, J_{Pt-C} = 24.6 Hz (PPh₃, ipso), 134.6 (m, PPh₃, ortho), 132.59, 132.01, $131.95 (d, J_{C-P} = 4.7 Hz), 131.5 (m), 131.32 (m), 131.02, 130.48$

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(s, PPh₃, para), 128.78 (d, $J_{C-P} = 9.8$, PPh₃, meta), 128.43 (t, $J_{C-P} = 5.1$ Hz) 127.79, 127.39, 78.28, 57.51, 30.58. HRMS (FAB) (m/e): calcd for (M + 1)⁺, 745.1948; found, 745.1980. Anal. Calcd for C₃₈H₃₂NOPPt: C, 61.29; H, 4.33; N, 1.88. Found: C, 61.43; H, 4.32; N, 1.84.

Preparation of Complex 12. To a Schlenk tube containing 5 (50 mg, 0.05 mmol) in 4 mL of THF was added HBr (16.2 mg, $12 \,\mu\text{L}$ of 30 wt % solution in acetic acid dissolved in 1 mL of THF) at room temperature. The color changed immediately from yellow to pale yellow. The mixture was stirred for 15 min at room temperature. Solvent was evaporated in vacuo, and the residue was dissolved in 3 mL of CH_2Cl_2 followed by addition of 10 mL of hexane. After 1 day off-white needles had formed: 35 mg (64%), mp 278-279 °C. IR (KBr): 3044 w, 2992 w, 1624, 1584, 1578, 1479, 1437, 1312, 750, 692, 524 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 9.15 (dd, 1H, ³J_{H-H} = 7.9 Hz, ⁴J_{H-H} = 1 Hz), 7.82 (d, 1H, ${}^{3}J_{H-H}$ = 7.6 Hz), 7.7 (d, 1H, ${}^{3}J_{H-H}$ = 8.2 Hz), 7.63 (t, 1H, ${}^{3}J_{H-H} = 7.6$ Hz), 6.9-7.55 (m, 34H, PPh₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 193.3, 137.46, 137.32, 137.14, 136.32, 135.39 (m, PPh₃), 134.32 (m, PPh₃), 132.5, 131.9, 131.34, 130.98, 130.23, 129.99, 129.7, 129.27, 129, 128.2, 128.05 (d), 126.67, 126.29. HRMS (FAB) (m/e): calcd for (M $(+1)^+$, 1004.1386; found, 1004.1402. Anal. Calcd for $C_{51}H_{39}$ -OP₂BrPt·1.5CH₂Cl₂: C, 55.69; H, 3.74. Found: C, 55.87; H, 3.81.

Preparation of Trimer 14. A Schlenk tube was charged with 5 (100 mg, 0.1 mmol), and 2 mL of C_6H_6 was added. To this solution was added tetracyanoethylene (30 mg, 0.234 mmol). The color changed immediately from yellow to brown. To this solution was added 5 mL of hexane. The solution was filtered through a short silica gel column using methylene chloride/hexane (7/3, v/v) as the eluent. Methylene chloride was evaporated in vacuum leaving yellow trimer 14 (9 mg, 45%). IR (KBr): 3058.7 w, 2957.6 w, 1696, 1590, 1289.2, 1261.5, 1246.2, 931.9, 800.1, 751, 733, 641.7 cm⁻¹. ¹H NMR (C₆D₆): δ 7.43 (dd, 6H, ${}^{3}J_{H4-H3} = 7.5$ Hz, ${}^{4}J_{H4-H2} = 1$ Hz, H4), 6.83 (d, 6H, ${}^{3}J_{H1-H2} = 7.9$ Hz, H1), 6.7 (td, 6H, ${}^{3}J_{H2-H1,3} = 7.5$ Hz, ${}^{4}J_{H2-H4} = 1$ Hz, H2), 6.49 (td, 2H, ${}^{3}J_{H3-H4,2} = 7.7$ Hz, ${}^{4}J_{H3-H1}$ = 1.4 Hz, H3). ${}^{13}C{}^{1}H$ NMR (C₆D₆): δ 197.42, 146.71, 138.18, 134.78, 133.15, 129.09, 127.93, 125.05. HRMS (FAB) (m/e): calcd for $(M + 1)^+$, 613.1804; found, 613.1835.

Preparation of Complex 15. To a solution of 6 (130 mg, 0.13 mmol) in 2 mL of benzene was added 22 mg (0.17 mmol) of TCNE at room temperature. After stirring of the mixture for 0.5 h, the solvent was evaporated in vacuo. The residue was dissolved in 5-10 mL of CH₂Cl₂, and 15 mL of hexane was added. The solution was kept at -20 °C for 2 days to give 82 mg (55%) of yellow-brown crystals. An analytically pure sample (off-white crystals) was obtained by recrystallization from CH₂Cl₂/hexane solution. Mp: 208 °C. IR (KBr): 3060 w, 2216 w, 1481, 1439, 1203, 1096, 744, 697 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 7.88 (dd, 1H, ${}^{3}J_{H4-H3} = 8.1$ Hz, ${}^{4}J_{H4-H2} = 1.4$ Hz, H4), 7.6 (dd, 1H, ${}^{3}J_{H5-H6} = 7.6$ Hz, ${}^{4}J_{H5-H7} = 1.5$ Hz, H5), 7.24 (td, 1H, ${}^{3}J_{H2-H1,3} = 8$ Hz, ${}^{4}J_{H2-H4} = 1.5$ Hz, H2), 7.09 (td, 1H, ${}^{3}J_{H3-H4,2} = 8$ Hz, ${}^{4}J_{H3-H1} = 1.4$ Hz, H3), 7 (dd, 1H, ${}^{3}J_{H1-H2}$ = 8 Hz, ${}^{4}J_{H1-H3}$ = 1 Hz, H1), 6.79 (td, 1H, ${}^{3}J_{H7-H6,8}$ = 7.7 Hz, ${}^{4}J_{\text{H7-H5}} = 1.3 \text{ Hz}, \text{H7}), 6.37 (d, 1\text{H}, {}^{3}J_{\text{H8-H7}} = 8.3 \text{ Hz}, \text{H8}), 6.32$ (td, 1H, ${}^{3}J_{H6-H5,7} = 7.5$ Hz, ${}^{4}J_{H6-H8} = 1.2$ Hz, H6), 7.1–7.56 (m, 30H, PPh₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 165.71 (d, J_{C-P} = 3.8 Hz), 164.37 (d, $J_{C-P} = 4.6$ Hz), 161.05, 157.78 (d, $J_{C-P} =$ 3.9 Hz), 135.93 (d, $J_{C-P} = 10.6 \text{ Hz}$, PPh₃), 134.44 (br), 131.43 (s, PPh₃), 130.93, 130.40, 130.22, 129.45, 128.81, 128.41 (d, $J_{\rm C-P} = 9.9$ Hz, PPh₃), 128.09, 126.81 (d, $J_{\rm C-P} = 6.1$ Hz), 124.58, 123.8, 120.78, 120.17, 117.89 (d, $J_{C-P} = 4.6$ Hz). HRMS (FAB) (m/e): calcd for $(M + 1)^+$, 1040.2247; found, 1040.2203. Anal. Calcd for C₅₆H₃₈N₄OP₂Pt•CH₂Cl₂: C, 60.86; H, 3.58; N, 4.98. Found: C, 60.55; H, 3.54; N, 4.92.

(Dibenzotropyne)bis(triphenylphosphine)platinum (16). To a solution of 7 (160 mg, 0.175 mmol) in 3 mL of CH_2 - Cl_2 was added dropwise at -78 °C triphenylcarbenium tetrafluoroborate (61 mg, 0.184 mmol) in 2 mL of CH_2Cl_2 . The resulting solution was stirred for 5 h at -78 °C and subsequently warmed slowly to room temperature. The resulting

Table 8. Fractional Coordinates and EquivalentIsotropica Thermal Parameters (Å2) for Non-HAtoms of Complex 15

			<u>+</u>	
atom	x	у	z	U
Pt	0.27993	0.01260(2)	0.08525	0.02981(8)
P1	0.2791(2)	0.0807(2)	-0.02475(14)	0.0344(8)
P2	0.3059(2)	0.1369(2)	0.15691(14)	0.0344(8)
0	0.2019(5)	-0.2173(6)	-0.0703(4)	0.051(3)
N1	0.1269(8)	-0.2217(8)	0.2398(6)	0.072(5)
N2	0.0695(6)	-0.0251(7)	0.0982(6)	0.053(3)
N3	0.2013(8)	-0.0033(7)	0.2943(6)	0.064(4)
N4	0.3705(8)	-0.1693(8)	0.2061(7)	0.066(5)
C1	0.2029(8)	-0.3253(7)	0.1027(7)	0.057(5)
C2	0.1873(8)	-0.4114(8)	0.0800(9)	0.064(5)
C3	0.1730(11)	-0.4249(9)	0.0088(10)	0.085(7)
C4	0.1779(9)	-0.3646(10)	-0.0398(9)	0.080(6)
C5	0.3249(9)	-0.2244(8)	-0.1288(6)	0.059(5)
C6	0.4009(9)	-0.2013(10)	-0.1332(8)	0.072(6)
C7	0.4346(8)	-0.1485(9)	-0.0824(8)	0.060(5)
C8	0.3910(8)	-0.1160(8)	-0.0271(7)	0.050(4)
C9	0.2669(6)	-0.1109(6)	0.0402(4)	0.031(3)
C10	0.2224(7)	-0.1668(6)	0.0742(5)	0.036(3)
C11	0.2064(7)	-0.2580(7)	0.0549(6)	0.043(4)
C12	0.1943(7)	-0.2802(7)	-0.0188(6)	0.046(4)
C13	0.3141(8)	-0.1389(7)	-0.0203(6)	0.043(4)
C14	0.2818(7)	-0.1942(7)	-0.0731(6)	0.047(4)
C15	0.1855(7)	-0.1255(6)	0.1400(5)	0.039(3)
C16	0.2538(6)	-0.0674(6)	0.1765(5)	0.034(3)
C17	0.1199(7)	-0.0665(7)	0.1154(6)	0.039(3)
C18	0.1530(8)	-0.1844(7)	0.1963(6)	0.047(4)
C19	0.2269(7)	-0.0297(7)	0.2434(6)	0.045(4)
C20	0.3199(9)	-0.1236(9)	0.1938(7)	0.052(5)
C21	0.2246(7)	0.1919(6)	0.1946(5)	0.036(3)
C22	0.2319(7)	0.2741(7)	0.2254(6)	0.047(4)
C23	0.1702(9)	0.3181(9)	0.2540(7)	0.067(5)
024	0.0984(9)	0.2807(9)	0.2010(0)	0.000(0)
020	0.0800(9)	0.2009(12)	0.2213(9) 0.1091(8)	0.070(7)
C20	0.1004(0) 0.2611(6)	0.1040(9)	0.1921(0) 0.1928(6)	0.030(3)
C31	0.3011(0)	0.2200(0) 0.2046(7)	0.1220(0) 0.0940(7)	0.037(3)
C32	0.3250(8)	0.2540(7)	0.0540(7)	0.068(6)
C34	0.3032(10)	0.3049(8)	0.0588(9)	0.000(0)
C35	0.4823(8)	0.3059(10)	0.1084(9)	0.002(1)
C36	0.4020(0)	0.2371(10)	0.1347(8)	0.010(0)
C41	0.3669(7)	0.0999(6)	0.2330(5)	0.000(0)
C42	0.4297(7)	0.0458(8)	0.2182(6)	0.048(4)
C43	0.4808(10)	0.0218(9)	0.2731(9)	0.071(6)
C44	0.4682(11)	0.0468(12)	0.3417(9)	0.083(7)
C45	0.4066(11)	0.0975(11)	0.3568(7)	0.080(6)
C46	0.3554(9)	0.1243(9)	0.3019(6)	0.062(5)
C51	0.2301(7)	0.0219(7)	-0.0981(5)	0.042(3)
C52	0.1498(9)	0.0174(8)	-0.1004(7)	0.057(5)
C53	0.1103(10)	-0.0214(9)	-0.1579(8)	0.067(5)
C54	0.1490(12)	-0.0577(9)	-0.2121(7)	0.076(6)
C55	0.2266(11)	-0.0563(9)	-0.2102(7)	0.071(6)
C56	0.2687(9)	-0.0166(8)	-0.1540(6)	0.060(4)
C61	0.3718(7)	0.1175(7)	-0.0602(6)	0.039(3)
C62	0.4371(8)	0.1194(9)	-0.0177(7)	0.047(5)
C63	0.5062(8)	0.1563(9)	-0.0403(7)	0.058(5)
C64	0.5083(9)	0.1872(8)	-0.1093(7)	0.066(5)
C65	0.4438(8)	0.1826(9)	-0.1534(7)	0.061(5)
C66	0.3757(7)	0.1472(8)	-0.1301(6)	0.050(4)
C71	0.2178(7)	0.1779(7)	-0.0234(6)	0.040(4)
C72	0.2318(8)	0.2501(7)	-0.0659(6)	0.048(4)
C73	0.1791(9)	0.3200(8)	-0.0684(8)	0.065(5)
074	0.1141(9)	0.3160(8)	-0.0275(9)	0.076(6)
U75	0.0994(11)	0.2448(12)	0.0101(9)	0.070(6)
1.(0	01024071	111(04(3)	UUU04(/)	(116) [(4)

^{*a*} For anisotropic atoms, the *U* value is U_{eq} , calculated as $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$, where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

very deep blue solution was filtered, and to the filtrate was added 15 mL of ether. After 2 h deep blue needles had formed. The solvent was removed by decantation, and the crystals (100 mg, 57%) were dried under vacuum. Mp: 197 °C dec. IR (KBr): 3057 w, 1654 w, 1648 w, 1436, 1084, 745, 694, 523 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 10.43 (s, 1H, H5), 8.78 (d, 2H, ³J_{H4-H3} = 8.3 Hz, H4), 7.94 (td, 2H, ³J_{H3-H4,2} = 8.3 Hz, ⁴J_{H3-H1} = 1.2 Hz, H3), 7.75 (td, 2H, ³J_{H2-H1,3} = 8.3 Hz, ⁴J_{H2-H4} = 1.2 Hz, H2),

7.55 (m, 12H, PPh₃, ortho), 7.4 (m, 6H, PPh₃, para), 7.25 (m, 12H, PPh₃, meta), 7.02 (d, 2H, ${}^{3}J_{\text{H1-H2}} = 8.3 \text{ Hz}$, H1). ${}^{13}\text{C}{}^{1}\text{H}$ NMR (CD₂Cl₂): δ 160.15 (dd, ${}^{2}J_{\text{C-Pcis}} = 4.04 \text{ Hz}$, ${}^{2}J_{\text{C-Ptrans}} = 84.03 \text{ Hz}$), 155.86, 140.2 (t, $J_{\text{C-P}} = 4.5 \text{ Hz}$), 139.5, 137.22, 135.39 (t, $J_{\text{C-P}} = 8.85 \text{ Hz}$), 134.74, 134.52 (p, ${}^{2}J_{\text{C-P}} = 6.4 \text{ Hz}$, PPh₃, ortho), 133.94 (d, ${}^{1}J_{\text{C-P}} = 49.72 \text{ Hz}$, PPh₃, ipso), 132.88, 131.08 (s, PPh₃, para), 129.04 (t, ${}^{3}J_{\text{C-P}} = 5.1 \text{ Hz}$, PPh₃, meta). ${}^{19}\text{F}$ NMR (CD₂Cl₂): δ -152.82. HRMS (FAB) (m/e): calcd for (M - BF₄)⁺, 908.2175; found, 908.220. Anal. Calcd for C₅₁H₃₈-BF₄P₂Pt· ${}^{1}/_{2}\text{CH}_{2}\text{Cl}_{2}$: C, 59.58; H, 3.88. Found: C, 59.31; H, 4.02.

Reaction of 16 with KBEt₃H. To a solution of **16** (30 mg, 0.03 mmol) in 3 mL of THF was added quickly KBEt₃H (35 μ L, 0.035 mmol of 1 M solution in THF) at room temperature. The color changed at once from deep blue to light yellow. After 5 min THF was removed in vacuum and the residue dissolved in CD₂Cl₂. ¹H and ³¹P{¹H} NMR showed formation of **7** in about 70% together with three minor platinum products which were not characterized.

Preparation of Complex 17. To a solution of 16 (100 mg, 0.1 mmol) in 3 mL of CH₂Cl₂ at room temperature was added 30 mg (0.7 mmol) of bis(dicyclohexylphosphino)ethane. The color changed immediately from deep blue to light yellow. After 15 min of stirring, 15 mL hexane was added causing pricipitation of an off-white solid. This solid was dissolved in 2 mL of CH_2Cl_2 , and 10 mL of Et_2O was added causing precipitation of 17 (80 mg, 66%). An analytically pure sample was obtained by recrystallization from CH₂Cl₂/hexane. Mp: 206-208 °C dec. IR (KBr): 3052, 2933, 2854, 1689, 1476, 1437, 1085 (br), 753, 694 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 7.71 (d, 4H, ³J_{H-H} = 7.5 Hz), 7.43 (m, 24H, PPh₃, ortho), 7.28 (m, 12H, PPh₃, para), 7.18 (m, 24H, PPh₃, meta), 6.74 (t, 4H, ${}^{2}J_{H-H} = 7.6$ Hz), 5.97 $(d, 4H, {}^{2}J_{H-H} = 6.2 \text{ Hz}), 5.64 (d, 2H, {}^{2}J_{P-H} = 19.8 \text{ Hz}), 2.95 (m, 2.95 \text{ m})$ 4H), 2.5 (m, 2H), 0.8–2 (m, 42H, $PCy_2).^{-13}C\{^1H\}$ NMR (CD₂-Cl₂): δ 136.48, 135.85, 134.46 (m, PPh₃), 133.45 (t, $J_{P-C} = 9.4$ Hz), 132.45, 130.11 (s, PPh₃), 129.66, 129.45, 128.66, 128.32 (m, PP h_3). 127.26 (m), 66.02, 51.71 (t, $J_{P-C} = 17.5$ Hz), 31.71 (br) 26.4–27.5 (m, PCy_2), 25.62. ^{19}F NMR (CD_2Cl_2): δ –148.3. Anal. Calcd for C₁₂₈H₁₂₆B₂F₈P₆Pt₂: C, 63.69; H, 5.26. Found: C, 63.39; H, 5.61.

Preparation of Complexes 18 and 19. To a solution of 16 (110 mg, 0.11 mmol) in 5 mL of CH_2Cl_2 was added HBr (27 μL of 30% HBr in acetic acid dissolved in 1 mL of $CH_2Cl_2)$ within 20 s. The color changed at once from deep blue to deep purple. The mixture was stirred for 5 min, and then the solvent was removed in vacuo. The residue was dissolved in 5 mL of CH₂Cl₂, and then 15 mL of hexane was added causing precipitation of 18. After 2 h at -16 °C the supernatent was discarded leaving 102 mg of product (85% yield). Mp: 268-269 °C dec. IR (KBr): 3053 w, 1602, 1514, 1480, 1435, 1384, 1095 br, 1055 br, 750, 695, 542, 525.5, 496 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 10.28 (d, 1H, J_{H-H} = 8.4 Hz), 9.97 (d, 1H, ${}^{4}J_{H-P}$ = 9 Hz, ${}^{3}J_{H-Pt} = 41.1$ Hz), 9.62 (s, 1H), 8.5 (m, 3H), 8.36 (s, 1H), 8.35 (s, 1H), 8.1 (t, 1H, ${}^{3}J_{H-H} = 7.2$ Hz), 8.04 (m, 1H), 6.8–7.6 (m, 30H, PPh₃). ${}^{13}C{}^{1}H$ NMR (CD₂Cl₂): δ 177.15, 164.98, 153.78, 152.37, 140.79, 140.24, 139.58, 137.75, 137.31, 136.34, 135.35 (d, $J_{C-P} = 10$ Hz), 134.51, 133.83 (d, $J_{C-P} = 11$ Hz), 132.43, 131.74, 131.55, 131.02, 130.34, 128.61 (d, $J_{C-P} = 10$ Hz), 127.68. ¹⁹F NMR (CD₂Cl₂): δ -152.5. HRMS (FAB) (m/ e): calcd for $(\mathrm{M}+1)^+,$ 988.1437; found, 988.1390. Anal. Calcd for C₅₁H₄₀BF₄BrP₂Pt: C, 57.00; H, 3.74. Found: C, 56.67; H, 3.82.

The sample was kept in CD_2Cl_2 for 1 month at room temperature. After that time the ¹H and ³¹P{¹H} showed

formation of **19** in about 75% with unreacted **18** and some decomposition products. ¹H NMR (CD₂Cl₂) spectroscopic data for **19**: δ 10.3 (d, 1H, $J_{H-H} = 8.2$ Hz), 9.64 (s, 1H), 9.45 (s, 1H, ³ $J_{H-Pt} = 70.2$ Hz), 8.25 (t of mult. 2H, $J_{H-H} = 7.6$ Hz), 7.77 (d, 1H, ³ $J_{H-H} = 8.1$ Hz), 8.5 (m, 2H), 8.1 (m, 2H), 6.8–7.6 (m, 30H, PPh₃).

Crystallographic Analysis. Crystal data and numerical details of the structures are given in Table 2. Data were collected at room temperature on a Siemens P3m/V diffractometer equipped with a graphite monochromator utilizing Mo Ka radiation ($\lambda = 0.710$ 73 Å). A total of 32 reflections with $20.0^{\circ} \le 2\theta \le 22.0^{\circ}$ were used to refine the cell parameters of each crystal. Four reflections were measured every 96 reflections to monitor instrument and crystal stability for each data set (maximum corrections on I were 4, 1, and 4% for 5, 14, and 15, respectively). Absorption corrections were applied based on measured crystal faces using SHELXTL plus.27 All of the three structures were refined in SHELXTL plus using full-matrix least squares. The structures of 5 and 15 were solved by the heavy-atom method in SHELXTL plus from which the locations of the Pt atoms were obtained. The rest of the non-hydrogen atoms were obtained from subsequent difference Fourier maps. All non-H atoms were refined with anisotropic thermal parameters, while positions of all of the H atoms were calculated in ideal positions and their isotropic thermal parameters were fixed. Methylene chloride was found along with the Pt complex in 15, and its non-H atoms were fully refined. In 5 disordered two partial toluene molecules were found and refined with isotropic thermal parameters. One of the toluene molecules (65% occupancy) is disordered in a general position, and the other (35% occupancy) is disordered around a center of inversion. The first toluene molecule was disordered in the methyl group only. While all of the ring C atoms were not disordered, two methyl groups of 32.5% occupancy were refined in para positions. The structure of 14 was solved by direct methods. The non-H atoms were refined with anisotropic thermal parameters, and the H atoms were located from a subsequent difference Fourier map and refined without any constraints. The linear absorption coefficients were calculated from values from the ref 28. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann²⁹ with anomalous-dispersion corrections from Cromer and Liberman,30 while those of hydrogen atoms were from Stewart, Davidson and Simpson.31

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Supplementary Material Available: Tables of atomic positions and U values, anisotropic thermal parameters for non-hydrogen atoms, and comprehensive bond lengths and angles (22 pages). Ordering information is given on any current masthead page.

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