Synthesis and Study of the (Ph₃P)₂Pt Complexes of Three Members of a Series of Highly Pyramidalized Alkenes

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The $(Ph_3P)_2Pt$ complexes (3) of three members of a homologous series of tricyclo[3.3, n.0^{3,7}]alk-3(7)-enes ($2\mathbf{a}-\mathbf{c}$) have been prepared by allowing these highly pyramidalized alkenes to displace ethylene from $(Ph_3P)_2PtC_2H_4$. The X-ray crystal structures of 3a-c show that pyramidalization angles at the carbons bonded to platinum increase from an average of $\phi =$ 48.3° in **3c** to $\phi = 55.1^\circ$ in **3b** to 62.3° in **3a**. In addition, as predicted computationally, the lengths of the bonds between the carbons attached to platinum increase and the C-Pt bond lengths decrease from 3c to 3a. The ¹H, ¹³C, ³¹P, and ¹⁹⁵Pt NMR spectra of 3a-c provide information about how pyramidalization at these carbons affects the electronic structures of the complexes. The changes in the ¹³C, ³¹P, and ¹⁹⁵Pt chemical shifts and also the changes in the ${}^{13}C - {}^{31}P$ and ${}^{31}P - {}^{31}P$ coupling constants are consistent with the expected increase in back-bonding from the HOMO of $(Ph_3P)_2Pt$ into the empty, π^* LUMO of the alkene as pyramidalization increases from 3c to 3a. The increase in the one-bond ${}^{13}C - {}^{195}Pt$ coupling constant from 3c to 3a is found to be linearly related to the decrease in the ³¹P-¹⁹⁵Pt coupling constant. This finding indicates that, with increasing pyramidalization, donation from the π HOMO of the alkene into the 6s orbital of platinum also increases but at the expense of donation into platinum 6s from the in-phase combination of phosphine lone pair orbitals.

A number of organic molecules, containing highly reactive π bonds, have been isolated as $(Ph_3P)_2Pt$ complexes. $(Ph_3P)_2Pt$ complexes of cycloalkynes that have bent triple bonds-cyclopentyne, cyclohexyne, and cycloheptyne,¹ two isomers of cycloheptadienyne,² and the tropylium analog of benzyne²-have been prepared. $(Ph_3P)_2Pt$ complexes of strained cyclic allenes, 1,2cycloheptadiene³ and 1,2,4,6-cycloheptatetraene,⁴ have also been isolated. Among the deformed alkenes that have been isolated as (Ph₃P)₂Pt complexes are torsionally strained bridgehead olefins that violate Bredt's rule,^{5.6} bicyclo[2.2.0]hex-1(4)-ene,⁷ and, most recently, fullerene (C_{60}) .^{8,9}

The spherical shape of C₆₀ causes each of the carbons in it to have a pyramidal, rather than planar, geometry. The effect of pyramidalization on the bonding in nonconjugated alkenes has been investigated, both computationally and experimentally.¹⁰ Ab initio calculations predict that pyramidalization should result in raising the energy of the π HOMO and lowering the energy of the π^* LUMO.¹¹ However, the increase in the energy of the HOMO is computed to be only a fraction of the size of the decrease in the energy of the LUMO. These computational predictions have recently been confirmed by PES and ETS experiments.¹²

The existence of a low-lying, unfilled, π^* orbital in an alkene would be expected to result in particularly strong back-bonding from a d^{10} metal, such as Pt(0).¹³ The results of ab initio calculations on the effect of olefin pyramidalization in the $(H_3P)_2Pt$ complex of ethylene give computational credibility to this qualitative prediction.¹⁴ Experimental confirmation might come from a study of the effects of increasing olefin pyramidalization on $(Ph_3P)_2Pt$ complexes of a homologous series of pyramidalized alkenes.

We have prepared such a series of tricyclo[$3.3.n.0^{3.7}$]alk-3(7)-enes (2a-c) with n = 1, 15, 2, 16 and 3, 12, 17 and we have reported in a preliminary fashion the synthesis and X-ray structure of the $(Ph_3P)_2Pt$ complex (3a) of $2a.^{18}$ In this paper we describe the preparation of the

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 $(Ph_3P)_2Pt$ complexes of **2b**,**c**, and we report the chemical shifts and coupling constants obtained from the ¹H, ¹³C, ³¹P, and ¹⁹⁵Pt NMR spectra of all three complexes (3a**c**).



Because 3a-c differ only in the degree to which the carbons bonded to platinum are forced to be pyramidalized, the NMR spectra of these three complexes provide detailed information about how pyramidalization of these carbons affects the electronic structures of the complexes. The differences in the chemical shifts and coupling constants, found in the ¹H, ¹³C, ³¹P, and ¹⁹⁵Pt NMR spectra of 3a-c, are discussed in this light. The X-ray structures of 3a-c, which are also reported, confirm that the changes in the chemical shifts and coupling constants can, in fact, be attributed to increased pyramidalization of the carbons bonded to platinum from 3c to 3a.

Results and Discussion

Preparation of the (Ph₃P)₂Pt Complexes. The synthesis of each complex was accomplished by reducing a diiodide $(1a, X = I)^{15}$ or dimesylate (1b, c, X = OMs)precursor with sodium amalgam and allowing the olefin (2) thus formed to displace ethylene from $(Ph_3P)_2$ - $PtC_2H_{4.}^{19}$ The generation and *in situ* trapping of **3a** by this method have already been described in a preliminary fashion.18

Alkene **2b** has been prepared previously by β -lactone pyrolysis;¹⁶ but for the purpose of trapping the olefin with $(Ph_3P)_2Pt$ to form 3b, the elevated temperatures required for decarboxylation of the β -lactone made development of a different method for generating 2b highly desirable. Therefore, ketoacetonide 4, an inter-



mediate in the synthesis of 2c,¹² was subjected to Wolff-Kishner reduction; and the acetonide group in the product (5) was then hydrolyzed to form diol 6. Reaction with methyllithium converted $\mathbf{6}$ to the dilithic salt.



Figure 1. ORTEP drawing of the X-ray structure of 3a. Hydrogens have been omitted for conciseness and clarity.

which, upon treatment with excess mesyl chloride afforded 1b, X = OMs. Reduction of this dimesylate with sodium amalgam in the presence of $(Ph_3P)_2PtC_2H_4$ gave 3b.

Unlike **2a**,**b**, **2c** is stable toward dimerization at room temperature. Therefore, it was not necessary to perform the sodium amalgam reduction of dimesvlate 1c, X =OMs, in the presence of $(Ph_3P)_2PtC_2H_4$. Instead, the dimesylate was first reduced and the olefin formed then added to a solution of $(Ph_3P)_2PtC_2H_4$ to yield **3c**.

Tetrasubstituted alkenes would not ordinarily be expected to form stable complexes with $(Ph_3P)_2Pt$.²⁰ In order to verify that it is the pyramidalization of the olefinic carbon atoms in 2a-c which allows these alkenes to form very stable complexes with $(Ph_3P)_2Pt$,²¹ the unbridged olefin, bicyclo[3.3.0]oct-1(5)-ene,^{22,23} was stirred overnight with $(Ph_3P)_2PtC_2H_4$. As expected, no trace of the (Ph₃P)₂Pt complex of bicyclo[3.3.0]oct-1(5)ene was detected.

X-ray Structures of the Complexes. The chemistry observed for alkenes 2a-c leaves little doubt that, as expected,¹¹ alkene pyramidalization increases as ndecreases.^{12,15-17} Nevertheless, in order to confirm experimentally that pyramidalization in the $(Ph_3P)_2Pt$ complexes of these alkenes also increases in the same order, we obtained X-ray structures of 3a-c.

The X-ray structure of 3a has been reported previously.¹⁸ However, despite the convergence of the final structure refinement to $R_f = 0.059$, the accuracy of the structure of the olefinic portion of the molecule was not completely satisfactory. For example, one allylic C-C bond length to an olefinic carbon was found to be 1.63-(4) Å, and the other was found to be 1.46(3) Å. One

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⁽²¹⁾ We have found 3a-c to be much more stable than the $(Ph_3P)_2$ -Pt complex of ethylene toward decomposition via alkene loss. This is not surprising, since the pyramidalized alkenes in these complexes are predicted to be much more strongly bonded to (Ph₃P)₂Pt than is ethylene.14

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Table 1. Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Coefficients (Å² $\times 10^3$) for 3a

atom	x	у	z	$U(eq)^a$
Pt	2491(1)	9590(1)	1291(1)	29(1)
C (1)	1609(10)	8406(5)	-286(5)	57(4)
C(2)	2532(16)	9068(4)	-232(3)	51(3)
C(3)	3009(8)	8979(4)	472 (4)	33(3)
C(4)	4197(11)	8430(6)	496 (6)	49 (4)
C(5)	3306(10)	7726(5)	465(4)	52(4)
C(6)	2375(15)	7891(3)	1041(4)	52(3)
C(7)	1865(9)	8649(4)	844(4)	34(3)
C(8)	729(11)	8531(7)	328(6)	54(5)
C(9)	2519(16)	7717(4)	-180(4)	53(3)
P(1)	1207(2)	9646(1)	2245(1)	31(1)
C(1P)	-461(8)	9177(4)	2192(4)	34(3)
C(2P)	-1142(8)	9183(5)	1590(5)	46 (3)
C(3P)	-2415(14)	8871(4)	1524(5)	58(3)
C(4P)	-3011(9)	8532(5)	2047(6)	59 (4)
C(5P)	-2342(13)	8506(5)	2644(6)	65(4)
C(6P)	-1079(9)	8829(5)	2713(5)	54(4)
C(7P)	2006(9)	9208(4)	2953(4)	35(3)
C(8P)	1738(9)	9355(4)	3607(4)	54(3)
C(9P)	2343(15)	8974(5)	4105(4)	73(4)
C(10P)	3228(12)	8426(7)	3964 (6)	84(5)
C(11P)	3544(13)	8265(7)	3312(5)	90(5)
C(12P)	2958(9)	8668(5)	2832(5)	58(4)
C(13P)	703(8)	10534(4)	2568(4)	36(3)
C(14P)	-587(9)	10830(5)	2410(5)	49 (4)
C(15P)	-852(10)	11547(5)	2560(6)	55(4)
C(16P)	122(11)	11961(5)	2871(6)	61(5)
C(17P)	1329(10)	11669(5)	3030(5)	50(4)
C(18P)	1644(9)	10955(4)	2888(4)	39(3)
P(2)	3923(2)	10564(1)	1298(1)	34(1)
C(19P)	5500(8)	10510(4)	779(4)	34(3)
C(20P)	6744(9)	10794(5)	971(5)	48(4)
C(21P)	7879(9)	10735(6)	567 (5)	59(4)
C(22P)	7812(9)	10400(6)	-43(5)	61(5)
C(23P)	6563(12)	10121(5)	-228(6)	67(5)
C(24P)	5418(11)	10177(5)	171(5)	50(4)
C(25P)	3164(11)	11412(7)	1017(7)	41 (4)
C(26P)	1747(12)	11520(7)	1129(6)	47(4)
C(27P)	1127(13)	12170(6)	944(6)	61(5)
C(28P)	1876(15)	12697(7)	637(7)	53(4)
C(29P)	3266(14)	12590(8)	521 (7)	59 (5)
C(30P)	3884(12)	11953(5)	719(6)	49(4)
C(31P)	4702(9)	10779(5)	2101(4)	35(3)
C(32P)	5226(11)	10227(5)	2469(5)	47(4)
C(33P)	5821(10)	10337(6)	3072(4)	62(4)
C(34P)	5862(9)	11011(6)	3334(5)	59 (4)
C(35P)	5318(11)	11580(7)	2996(5)	56 (4)
C(36P)	4752(9)	11479(5)	2364(5)	45 (4)

^{*a*} Equivalent isotropic U defined as one-third of the trace of the orthogonalized \mathbf{U}_{ij} tensor.

would have expected both bonds to have lengths that were nearly the same and approximately the average of these two different bond lengths.

In order to see if another independent structure determination would produce better results, we prepared **3a** again. Crystals were grown, the X-ray data recollected, and the structure solved again. After refinement $R_f = 0.0275$ was obtained; and although some pairs of allylic C-C bond lengths still differed by as much as 0.04 Å, the results of this determination of the structure of **3a** were definitely an improvement over the previous one.¹⁸

An ORTEP drawing of the structure of 3a is shown in Figure 1. Table 1 gives the refined atomic coordinates and isotropic displacement coefficients, and Table 4 gives the values of important bond lengths and bond angles that were obtained from the redetermination of the structure of 3a. The values in Table 4 agree well



Figure 2. ORTEP drawings of the X-ray structures of the two independent molecules of **3b** in the unit cell. Hydrogens have been omitted for conciseness and clarity.

with those found previously.¹⁸ A complete listing of all the bond lengths and bond angles, obtained from the redetermination of the structure of 3a, is available as supporting information.²⁴

Crystals of **3b** were found to contain two independent molecules in the unit cell. As shown in Figure 2, the two molecules differ in the way the two triphenylphosphine groups in each are oriented. Table 2 lists the refined atomic coordinates and isotropic displacement coefficients for both molecules, and the values of important bond lengths and bond angles in both are given in Table 4. The remaining bond lengths and bond angles in **3b** can be found in the supporting information.²⁴

The X-ray structure obtained for **3c** was better than those obtained for either **3a** or **3b**. Refinement converged to $R_f = 0.0195$, and bond lengths and bond angles that should have been nearly the same were generally found to be identical to within the precision of the structure determination. Table 3 provides the refined

⁽²⁴⁾ Ordering information is given on any current masthead page.

Table 2.	Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Coefficients (A	$Å^2 \times$	10 ³) for
	Both Molecules of 3b in the Unit Cell		

atom	x	γ	z	$U(eq)^a$	atom	x	ν	<i>z</i>	U(ea)a
Pt	-1923(1)	2863(1)	2160(1)	33(1)	Pt'	3125(1)		2675(1)	32(1)
$\hat{\mathbf{C}}(1)$	-1464(10)	4633(6)	2896(5)	75(5)	$\tilde{C}(1')$	3929(9)	-3989(7)	1487(5)	72(5)
$\mathbf{C}(2)$	-1902(8)	3707(5)	3266(4)	58(4)	C(2')	3326(8)	-3120(7)	1348(5)	65(5)
C(3)	-1163(7)	3255(5)	2823(4)	41(3)	C(3')	3962(7)	-2716(6)	1729(4)	45(4)
$\mathbf{C}(4)$	9(7)	2860(6)	3034(5)	59(4)	C(4')	4979(9)	-2129(8)	1328(6)	40(4) 80(6)
C(5)	869(9)	3595(8)	2584(6)	83(6)	C(5')	6003(8)	-2773(8)	1467(6)	85(G)
C(6)	415(8)	3866(7)	1909(5)	76(5)	C(6')	5651(7)		2227(5)	79(6)
C(0)	-009(7)	3889(5)	9144(4)	45(3)	C(7')	4940(7)	-3437(5)	2207(0)	15(0)
$\mathbf{C}(\mathbf{R})$	-1449(10)	4734(6)	2144(4)	79(5)	$C(\mathbf{r}')$	4040(1) 3057(0)	-4970(6)	2012(4)	40(4)
C(0)	-1442(10) -948(19)	4734(0)	2102(3)	119(9)	C(0')	5150(10)	-2018(10)	1057(7)	119(9)
C(9)	-240(13) 949(11)	4744(0)	3034(7) 3950(6)	05(7)	C(9)	6191(0)		1007(7)	113(0)
$\mathbf{D}(1)$	040(11)	4303(9) 2005(1)	1097(1)	90(7) 96(1)	$\mathbf{D}(10)$	0101(9)	~3347(9)	1044(0)	90(7)
$\Gamma(1)$	-2201(2)	4091(5)	506(4)	30(1)	F(3)	2011(2)		3041(1)	31(1)
$C(\mathbf{1P})$	-2397(0)	4431(3)	020(4) 501(4)	39(3)	C(37P)	3209(0)	-4250(5)	4323(4)	41(3)
C(2P)	-1007(7)	4010(0) ECTE(E)	001(4)	50(4)		0940(0) 4955(0)	-4739(0)	3992(3)	62(4)
C(3P)	-1602(8)	0070(0) 5020(5)	03(4)	00(4)	C(39P)	4200(9)	-000000	4374(6)	75(5)
C(4P)	-2431(7)	5960(5)	-358(4)	49(4)	C(40P)	3939(9)	-5928(6)	5058(6)	66(5)
C(5P)	-3237(8)	5363(5)	-330(4)	54(4)	C(41P)	3279(8)	-5453(7)	5376(5)	70(5)
C(6P)	-3227(7)	4519(5)	102(4)	49(4)	C(42P)	2917(8)	-4613(5)	5034(4)	56(4)
C(7P)	-1082(6)	2735(5)	552(4)	39(3)	C(43P)	3785(6)	-2525(4)	4131(3)	33(3)
C(8P)	-1001(8)	2996(6)	-149(4)	54(4)	C(44P)	3677(7)	-2579(5)	4808(4)	45(3)
C(9P)	-72(9)	2707(7)	-530(5)	71(5)	C(45P)	4432(7)	-2094(5)	4979(4)	51(4)
C(10P)	749(9)	2162(7)	-202(6)	73(5)	C(46P)	5292(7)	-1593(5)	4503(4)	51(4)
C(11P)	691(9)	1898(6)	501(6)	70(5)	C(47P)	5428(7)	-1548(5)	3831(4)	47(3)
C(12P)	-235(7)	2192(5)	864(4)	52(4)	C(48P)	4684(6)	-2009(5)	3659(4)	37(3)
C(13P)	-3582(6)	2596(5)	1029(4)	38(3)	C(49P)	1389(6)	-3107(5)	4302(4)	38(3)
C(14P)	-3586(8)	2015(6)	701(4)	52(4)	C(50P)	989(7)	-2538(5)	4617(4)	48 (4)
C(15P)	-4638(9)	1634(6)	723(5)	68(5)	C(51P)	-127(8)	-2573(7)	4969 (4)	62(4)
C(16P)	-5651(9)	1833(6)	1038(6)	75(5)	C(52P)	-890(9)	-3190(8)	4996(5)	78(5)
C(17P)	-5686(8)	2434(7)	1365(5)	69 (5)	C(53P)	-527(8)	-3769(7)	4682(6)	85(6)
C(18P)	-4631(7)	2788(5)	1357(4)	48(4)	C(54P)	615(7)	-3726(6)	4334(5)	67(5)
P(2)	-2907(2)	1607(1)	2816(1)	34(1)	P(4)	1844(2)	-1551(1)	2356(1)	33(1)
C(19P)	-2263(6)	911(5)	3550(3)	33(3)	C(55P)	2018(7)	-961(5)	1428(4)	41(3)
C(20P)	-2033(7)	38(5)	3693(4)	47(4)	C(56P)	1256(9)	-995(6)	1016(4)	64(4)
C(21P)	-1568(8)	-463(6)	4271(4)	59(4)	C(57P)	1484(10)	-548(7)	316(5)	79(5)
C(22P)	-1340(7)	-103(5)	4711(4)	48(4)	C(58P)	2492(10)	-51(7)	29(5)	74(5)
C(23P)	-1591(8)	761(6)	4583(4)	59(4)	C(59P)	3251(9)	-11(7)	423(5)	76(5)
C(24P)	-2046(8)	1252(5)	4020(4)	48(3)	C(60P)	3010(8)	-456(6)	1111(4)	66(4)
C(25P)	-4375(7)	1777(5)	3253(4)	41(3)	C(61P)	326(6)	-1957(5)	2609(4)	39(3)
C(26P)	-4792(8)	2612(6)	3059(5)	60(4)	C(62P)	-485(7)	-1711(5)	3071(4)	51(4)
C(27P)	-5009(7)	1116(6)	3769(4)	55(4)	C(63P)	-1623(8)	-2052(6)	3281(5)	68(5)
C(28P)	-6115(8)	1270(8)	4063(5)	72(6)	C(64P)	-1931(8)	-2633(6)	3016(5)	67(5)
C(29P)	-6554(9)	2076(10)	3875(7)	87(7)	C(65P)	-1141(8)	-2907(6)	2580(5)	66(4)
C(30P)	-5922(9)	2756(8)	3381(6)	80(6)	C(66P)	4(8)	-2574(6)	2382(5)	59(4)
C(31P)	-3175(7)	831(5)	2429(4)	42(3)	C(67P)	1777(6)	-623(4)	2632(4)	35(3)
C(32P)	-2196(7)	518(5)	2099(4)	51(4)	C(68P)	2375(7)	-631(5)	3131(4)	44(3)
C(33P)	-2314(10)	-115(6)	1837(5)	66(5)	C(69P)	2363(9)	54(6)	3347(5)	68(5)
C(34P)	-3384(10)	-426(6)	1882(5)	72(5)	C(70P)	1752(9)	776(6)	3056(5)	68(5)
C(35P)	-4364(9)	-81(6)	2155(4)	58(4)	C(71P)	1140(10)	818(6)	2558(5)	81(5)
C(36P)	-4261(8)	542(5)	2434(4)	46(3)	C(72P)	1188(9)	129(6)	2329(5)	69(5)
					U() == /	1100.07	1000/		00(0)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized \mathbf{U}_{ij} tensor.

atomic coordinates and isotropic displacement coefficients. Important bond lengths and bond angles are given in Table 4, and the remainder are available as supporting information.²⁴

The ORTEP drawings of the structures of 3a-c, shown in Figures 1–3, clearly reveal that pyramidalization of the carbons bonded to Pt in these complexes does, indeed, increase as *n* decreases. A convenient measure of the degree to which an olefin is pyramidalized is the pyramidalization angle, ϕ , which is defined as the angle between the extension of the bond between the olefinic carbons and the plane containing one of these carbons and the two substituents attached to it.¹⁰ The pyramidalization angles at C(3) and C(7) in each complex are given in Table 4. The average values of ϕ for 3a-c are respectively 62.3, 55.1, and 48.3°. These values provide quantitative confirmation that, as indicated qualitatively by the drawings in Figures 1–3, olefin pyramidalization decreases from **3a** to **3c**.

Calculations on a $(Ph_3P)_2PtC_2H_4$ model predict that increased olefin pyramidalization in **3** should be accompanied by a decrease in the Pt-C bond lengths, an increase in the length of the C-C bond between the olefinic carbons, and little change in the P-Pt bond length or the P-Pt-P bond angle.¹⁴ Table 4 shows that these predictions compare well with experiment.

With the exception of one long P-Pt bond in 3a, the P-Pt bond lengths do seem to remain quite constant in 3a-c. Although the P-Pt-P bond angles appear to vary slightly, there is no obvious trend, since the two different molecules of 3b each have a smaller P-Pt-P bond angle than either 3a or 3c. The 3.1° difference between the P-Pt-P bond angles in the two molecules of 3b in the same crystal suggests that the differences found between the P-Pt-P bond angles in 3a-c are not structurally significant.

As predicted,¹⁴ the C-Pt bond lengths in **3** do decrease with increased pyramidalization. The decrease could be due to stronger bonding between the olefin and platinum and/or to a decrease in steric repulsion between the allylic CH₂ groups and the $(Ph_3P)_2Pt$ moiety as pyramidalization increases. The fact that the C-Pt

Table 3. Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Coefficients $(\mathring{A}^2 \times 10^3)$ for 3c

atom	x	у	z	$U(eq)^a$
Pt	1849(1)	2582(1)	2202(1)	31(1)
C(1)	-1381(4)	1227(4)	407(4)	53 (2)
C(2)	-935(4)	1503(4)	1534(4)	49(2)
C(3)	-60(4)	2645(4)	1781(3)	35(2)
C(4)	-392(5)	3790(4)	2122(4)	50(2)
C(5)	-685(5)	4328(5)	1205(4)	57(2)
C(6)	242(5)	3953(4)	772(4)	50(2)
C(7)	352(4)	2771(4)	989(3)	36(2)
C(8)	-232(5)	1717(5)	203(4)	49 (2)
C(9)	-2517(5)	1755(5)	-84(4)	70(3)
C(10)	-2738(5)	2854(6)	419(5)	77(3)
C(11)	-2023(5)	3992(5)	522(5)	66(3)
$\mathbf{P}(1)$	3490(1)	2725(1)	1705(1)	36(1)
C(1P)	3177(4)	2199(4)	409(3)	41(2)
C(2P)	2340(4)	2698(5)	-258(4)	52(2)
C(3P)	2045(5)	2345(5)	-1233(4)	61(2)
C(4P)	2584(6)	1499(6)	-1569(4)	74(3)
C(5P)	3432(6)	1034(5)	-938(4)	65(3)
C(6P)	3744(5)	1392(5)	66(4)	57(2)
C(7P)	4183(4)	4202(4)	1813(3)	41(2)
C(8P)	4937(4)	4518(5)	1307(4)	52(2)
C(9P)	5382(5)	5653(5)	1353(4)	63(3)
C(10P)	5039(6)	6490(5)	1891(4)	67(3)
C(11P)	4293(6)	6189(5)	2390(4)	67(3)
C(12P)	3864(5)	5060(4)	2347(4)	51(2)
C(13P)	4760(4)	2004(5)	2282(3)	48(2)
C(14P)	5983(5)	2498(6)	2659(4)	73(3)
C(15P)	6870(7)	1905(8)	3095(5)	92(4)
C(16P)	6556(9)	806(10)	3151(5)	110(5)
C(17P)	5331(9)	259(7)	2781(6)	101(5)
C(18P)	4430(6)	861(5)	2329(5)	70(3)
P(2)	2464(1)	2204(1)	3732(1)	36(1)
C(19P)	1908(4)	2980(4)	4614(3)	40(2)
C(20P)	2653(5)	3513(5)	5547(4)	57(2)
C(21P)	2135(6)	4056(5)	6160(4)	73(3)
C(22P)	917(6)	4061(5)	5879(4)	60(3)
C(23P)	149(5)	3524(5)	4955(4)	57(2)
C(24P)	636(5)	2989(4)	4326(4)	48(2)
C(25P)	1834(4)	720(4)	3709(3)	40(2)
C(26P)	1557(5)	371(5)	4474(4)	51(2)
C(27P)	990(5)	-751(5)	4380(5)	62(3)
C(28P)	734(5)	-1518(5)	3546(4)	58(2)
C(29P)	1045(5)	-1201(4)	2792(4)	57(2)
C(30P)	1579(4)	-68(4)	2870(4)	47(2)
C(31P)	4114(4)	2399(4)	4467(3)	44(2)
C(32P)	4853(4)	3402(5)	4492(4)	52(2)
C(33P)	6083(5)	3642(5)	5045(4)	64(3)
C(34P)	6604(5)	2829(5)	5529(4)	67(3)
C(35P)	5914(5)	1821(5)	5492(4)	65(3)
C(36P)	4657(5)	1594(4)	4956(4)	50(2)

^{*a*} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized \mathbf{U}_{ij} tensor.

bond length in the $(Ph_3P)_2Pt$ complex of ethylene (2.11 Å)²⁵ is actually slightly shorter than the average of those in the more highly pyramidalized²⁶ complex of **2c** (2.12 Å) indicates that steric effects probably do have some influence on C-Pt bond lengths.

The amount of bonding between platinum and a complexed alkene does not appear to have a profound effect on the C-Pt bond length. These bond lengths are nearly the same in the $(Ph_3P)_2Pt$ complexes of ethylene $(2.11 \text{ Å})^{25}$ and TCNE $(2.10 \text{ Å})^{27}$ despite the 32 kcal/mol stronger platinum-olefin bond in the latter.²⁸ The

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) Obtained from the X-ray Structures of 3a-c

	3a	3b	3b ′ ^{<i>a</i>}	3c
Pt-P(1)	2.298(2)	2.284(2)	2.283(2)	2.274(1)
Pt-P(2)	2.279(2)	2.266(2)	2.272(2)	2.276(1)
Pt-C(3)	2.068(8)	2.105(9)	2.086(8)	2.129(4)
Pt-C(7)	2.056(8)	2.115(8)	2.095(8)	2.113(4)
C(3) - C(7)	1.475(11)	1.441(9)	1.467(9)	1.421(7)
C(2) - C(3)	1.503(11)	1.527(12)	1.539(14)	1.536(6)
C(3) - C(4)	1.539(13)	1.521(10)	1.504(10)	1.539(7)
C(6) - C(7)	1.541(11)	1.520(11)	1.517(11)	1.520(6)
C(7) - C(8)	1.535(13)	1.522(11)	1.527(13)	1.521(5)
P(1) - Pt - P(2)	106.8(1)	103.1(1)	106.2(1)	108.7(1)
$\phi(3)^b$	60.4(14)	55.4(12)	53.0(12)	47.8(8)
C(2)-C(3)-C(4)	109.5(8)	116.7(7)	115.4(7)	122.6(4)
C(2) - C(3) - C(7)	107.2(8)	107.2(6)	108.1(7)	109.6(3)
C(4) - C(3) - C(7)	105.9(7)	107.5(6)	109.4(6)	108.0(4)
$\phi(7)^b$	64.2(14)	53.5(12)	58.3(12)	48.8(8)
C(6)-C(7)-C(8)	106.1(8)	118.2(7)	115.8(7)	120.8(4)
C(3)-C(7)-C(6)	105.6(8)	107.7(6)	106.2(6)	109.5(4)
C(3)-C(7)-C(8)	104.7(7)	107.9(6)	106.2(7)	108.4(4)

^a Second independent molecule in the unit cell. ^b The pyramidalization angle, $\phi(n)$, at C(n) (n = 3 and 7) is defined¹⁰ as the angle between the C(n - 1)-Cn-C(n + 1) plane and the extension of the C(3)-C(7) bond.



Figure 3. ORTEP drawing of the X-ray structure of 3c. Hydrogens have been omitted for conciseness and clarity.

greater steric requirements of a cyano group, compared to a hydrogen atom, may tend to equalize the C-Pt bond lengths in these two complexes.

The C-C bond length in the $(Ph_3P)_2Pt$ complex of ethylene (1.43 Å) is about 0.06 Å shorter than that between the olefinic carbons in the $(Ph_3P)_2Pt$ complex of TCNE. The longer olefinic C-C bond in the latter complex has been attributed to the greater back-bonding in it between a filled metal d orbital and the empty π^* orbital with which it interacts.²⁸

An increase of 0.08 Å in the C-C bond length in the $(H_3P)_2Pt$ complex of ethylene has also been computed for a $(H_3P)_2PtC_2H_4$ model for 3a,¹⁴ and a difference of 0.05 Å has been calculated between this bond length in

⁽²⁵⁾ Cheng, P. T.; Nyburg, S. C. Can. J. Chem. 1972, 50, 912.

⁽²⁶⁾ It is known that planar alkenes pyramidalize upon coordination to transition metals.²⁰ Although the X-ray structure of the (Ph₃P)₂Pt complex of ethylene has been published,²⁵ the hydrogen atoms were not located, so that the degree of pyramidalization at carbon in this complex is not known. However, in the optimized geometry of (H₃P)₂-PtC₂H₄, obtained from *ab initio* calculations,¹⁴ the pyramidalization angle, ϕ (the angle between the H–C–H plane and the extension of the C-C bond), is 27.1°.

⁽²⁷⁾ Panattoni, C.; Bombieri, G.; Belluco, U.; Baddley, W. H. J. Am. Chem. Soc. **1968**, 90, 798. Bombieri, G.; Forsellini, E.; Panattoni, C.; Graziani, R.; Bardoli, G. J. Chem. Soc. A **1970**, 1313.

⁽²⁸⁾ Evans, A.; Mortimer, C. T.; Puddephat, R. J. J. Organomet. Chem. 1974, 72, 295.

the $(H_3P)_2PtC_2H_4$ models for **3a**,c.²⁹ As predicted from these calculations on models, the data in Table 4 do show an increase in the C-C bond lengths between the olefinic carbons in 3 with increasing pyramidalization. The difference between the length of the C(3)-C(7) bond in 3c and 3a, is, within experimental error, the same as the 0.05 Å difference computed between the bond lengths in the models.

The pyramidalization angles at C(3) and C(7) in **3c** are not required to be exactly the same, even in the gas phase, but they differ by only 1.0° in the crystal. This is smaller than the 3.8° difference between the pyramidalization angles at C(3) and C(7) in the crystal of **3a**. The latter pyramidalization angles would, of course, be expected to be identical in gas-phase molecules of 3a.

In contrast to the $(Ph_3P)_2Pt$ complex of 2c (3c), the 10-methyl-10-selenonia analog of olefin 2c shows an 8° difference between the values of ϕ (20.3 and 12.3°) at C(3) and C(7).³⁰ In both compounds the less pyramidalized carbon is found syn to the three-atom bridge.

Since olefin **2c** is computed to have nearly identical values of ϕ (25.2 and 25.0°),¹¹ it has been suggested that the 8° difference in the values of ϕ at the olefinic carbons in the selenonium salt is due to an attraction between the positively charged selenium atom and the π electrons at the doubly-bonded carbon syn to it.^{11,31} The very small difference between the values of ϕ at the much more highly pyramidalized olefinic carbons in $(Ph_3P)_2Pt$ complex **3c** tends to support this suggestion.

The most important result of the determinations by X-ray crystallography of the structures of 3a-c is the confirmation of the expected increase in pyramidalization angle, ϕ , with decreasing n in these $(Ph_3P)_2Pt$ complexes. This enabled us to interpret the changes in the NMR spectra of the complexes in terms of the changes in the geometry and the electronic structure of the alkene moiety that an increase in ϕ produces.^{11,12}

¹H NMR Spectra of the Complexes. The assignments of the resonances in the ¹H spectrum of **3a** were straightforward, except for determining which of the four-proton resonances belonged to the pseudoaxial protons (H_{ax}) of the six-membered rings and which belonged to the pseudoequatorial protons (H_{eq}) . This assignment was made on the basis of an NOE experiment in which the methylene protons of the one-carbon bridge at δ 2.06 were irradiated. The much greater enhancement observed for the four protons at δ 2.20 than for those at δ 2.37 identified the former as being pseudoaxial and the latter as being pseudoequatorial.

This assignment is consistent with the observation that axial protons generally appear at higher field than equatorial protons.³² It is also consistent with the finding that, as shown in Table 5, the protons at δ 2.20 show very weak coupling to ¹⁹⁵Pt, whereas those at δ 2.37 exhibit a coupling constant of 52.2 Hz. Inspection of a model of **3a** shows that the dihedral angle between a pseudoaxial C-H bond and the adjacent C-Pt bond

Table 5. ¹H Chemical Shifts (ppm) and J_{H-Pt} Coupling Constants (Hz) for 3a-c

complex	d _{Hax}	³ J _{Hax-Pt}	δ_{Heq}	${}^3J_{\rm Heq-Pt}$	δ_{Hbh}	${}^4J_{\rm Hbh-Pt}$
3a ^a	2.20	<10	2.37	52.2	3.46	60.3
$\mathbf{3b}^a$	1.84	13.8	2.47	69.3	2.97	39.1
$\mathbf{3c}^{b}$	2.36/2.10	20.1	2.88/2.54	80.6	2.80	<20

^a Benzene-d₆, 298 K. ^b Toluene-d₈, 245 K.

is close to 90°, but the pseudoequatorial C-H and C-Ptbonds are more nearly eclipsed. Therefore, the Karplus relationship for three-bond coupling constants³³ predicts small $^{195}Pt-^{1}H$ coupling for H_{ax} and large $^{195}Pt-^{1}H$ coupling for H_{eq} in **3a**.

The largest ¹⁹⁵Pt-¹H coupling constant in this complex is for the two bridgehead protons (H_{bh}). A model shows the existence of a "W" relationship between each of the bridgehead C-H bonds and both of the C-Pt bonds. This type of spatial relationship generally leads to large coupling constants.³⁴ The chemical shift of H_{bh} is also rather low, further suggesting the possibility of some interaction between the bridgehead C-H and the C-Pt bonds.

In the ¹H NMR spectrum of the (Ph₃P)₂Pt complex of 2b the resonance for Hax is found about 0.4 ppm upfield from those in the complexes of 2a or 2c. This upfield position of the H_{ax} resonance is not unique to 3b but seems to be a general feature of the tricyclo[3.3.2.0^{3.7}]decane skeleton. For example, the Hax resonance in acetonide 5 is found at δ 1.88, 0.37 ppm upfield from that in the homologous acetonide precursor of 2c.¹²

The H_{eq} resonance in 5, which appears at δ 2.16, is also upfield from that in the acetonide precursor of 2c.12 The difference in chemical shift is 0.18 ppm, and a similar difference in chemical shift is found between H_ in **3b.c.** Therefore, the data in Table 5 indicate that the $(Ph_3P)_2Pt$ group in 3a-c does not have a dramatic effect on the chemical shifts of H_{ax} and H_{eq} in the complexed alkenes.

The upfield position of the resonance for H_{ax} in **3b** causes H_{ax} to have essentially the same chemical shift as the four protons of the ethano bridge. Consequently, it was difficult to extract the ${}^{1}H_{ax} - {}^{195}Pt$ coupling constant from the ¹H NMR spectrum. Therefore, the ¹H-¹⁹⁵Pt NMR spin echo difference (SED) spectrum³⁵ of **3b** was obtained.

In a ${}^{1}\text{H}-{}^{195}\text{Pt}$ SED spectrum only those protons that are coupled to ¹⁹⁵Pt appear. In the SED spectrum of **3b**, the resonance for H_{ax} appeared as a triplet with J = 13.8 Hz, indicating that the three-bond ${}^{1}H_{ax} - {}^{195}Pt$ and the geminal ${}^1H_{ax} - {}^1H_{eq}$ coupling constants are both about this size.

The $(Ph_3P)_2Pt$ complex of **3c**, like the olefin from which it is formed and other derivatives of tricyclo- $[3.3.3.0^{3.7}]$ undecane, undergoes a conformational change, involving flipping of the trimethylene bridge.³⁶ In the 500 MHz ¹H NMR spectrum of **3c**, this process is frozen out at 245 K, so that two different sets of pseudoaxial and pseudoequatorial protons can be observed at this temperature. On warming, coalescence occurs around 300 K, giving $\Delta G^{\ddagger} \approx 14$ kcal/mol.³⁶ The chemical shifts

⁽²⁹⁾ RHF optimization of the geometry of $(H_3P)_2PtC_2H_4$ with the yramidalization angle frozen at $\phi = 49.0^{\circ}$: Hrovat, D. A.; Borden, T. Unpublished results.

⁽³⁰⁾ Hrovat, D. A.; Miyake, F.; Trammell, G.; Gilbert, K. E.; Mitchell, J.; Clardy, J.; Borden, W. T. J. Am. Chem. Soc. **1987**, 109, 5524. (31) For a discussion of and leading references to interactions between cations and π bonds, see: Kearney, P. C.; Mizoue, L. S.; Kumpf, R. A.; Forman, J. E.; McCurdy, A.; Dougherty, D. A. J. Am. Chem. Soc. 1993, 115, 9907.

⁽³²⁾ See, for example: Günther, H. NMR Spectroscopy, An Introduction; Wiley: New York, 1980; p 72.

⁽³³⁾ See, for example, p 106 of ref 32.

 ⁽³⁴⁾ See, for example, pp 115-116 of ref 32.
 (35) Emshwiller, M.; Hahn, E. L.; Kaplan, D. Phys. Rev. 1959, 118, 414.

⁽³⁶⁾ Smith, J. M.; Hrovat, D. A.; Borden, W. T. Tetrahedron Lett. 1993, 34, 5991.

Table 6. ³¹P and ¹⁹⁵Pt Chemical Shifts (ppm) and ¹J_{P-Pt} Coupling Constants (Hz) for 3a-c and for $(Ph_3\hat{P})_2PtC_2H_4$ in Benzene- d_6 at 25 °C

complex		δpt ^b	${}^{1}J_{P-Pt}$
3a	30.5	-467	2960
3b	31.1	-514	3115
3c (Ph ₃ P) ₂ PtC ₂ H₄	$32.2 \\ 34.1$	$-501 \\ -555$	3332 3740
(0.00- /0 04			

^a Relative to 85% H₃PO₄. ^b ∂_{Pt} in **3a-c** was measured relative to δ_{Pt} in $(Ph_3P)_2PtC_2H_4$, for which δ_{Pt} was taken from ref 38.

and coupling constants from the low-temperature spectrum, taken at 245 K, are given in Table 5.

Proton decoupling and use of the SED pulse sequence allowed all the resonances in the 500 MHz ¹H NMR spectrum of 3c at both 245 and 338 K to be assigned and the ¹H-¹⁹⁵Pt coupling constants to be measured. The SED experiment confirmed that the bridgehead protons are coupled to ¹⁹⁵Pt. However, a single broad resonance for these protons was observed in the SED spectrum, so that the precise ¹H_{bh}-¹⁹⁵Pt coupling constant could not be obtained. The entry for this coupling constant in Table 5 is an upper limit, based on the width of H_{bh} peak in the SED spectrum and the absence of detectable splitting in it. The same is true of the entry for the ${}^{1}H_{ax} - {}^{195}Pt$ coupling constant in **3a**.

Table 5 shows that from 3a to 3c the ${}^{1}H_{ax} - {}^{195}Pt$ and $^1\mathrm{H}_\mathrm{eq}\mathrm{-}^{195}\mathrm{Pt}$ coupling constants both increase but the $^1\mathrm{H}_\mathrm{bh}$ -95Pt coupling constant decreases. Molecular models indicate that these changes in the ¹H-¹⁹⁵Pt coupling constants can be attributed to the changes in the geometry of the carbon skeleton of 3, rather than to changes in the C-Pt bonding.

From **3a** to **3c** the five-membered rings flatten, so that the dihedral angle between the pseudoequatorial C-H bonds and the C-Pt bonds moves closer to zero. This change is presumably responsible for the monotonic ${}^{1}\mathrm{H}_{\mathrm{eq}}$ increase in the ¹⁹⁵Pt coupling constant. Flattening of the five-membered rings also increases the dihedral angle between the pseudoaxial C-H bonds and the C-Pt bonds past 90°, which is probably why, although the ${}^{1}H_{ax} - {}^{195}Pt$ coupling constant remains small, it too increases monotonically. Finally, the "W" relationship between the bridgehead C-H and the C-Pt bonds is lost as the rings flatten. For this reason the ¹⁹⁵Pt-¹H_{bh} coupling constant would be expected to decrease with increasing n, as is observed.

³¹P and ¹⁹⁵Pt NMR Spectra of the Complexes. The data obtained from the ³¹P and ¹⁹⁵Pt NMR spectra of 3a-c are contained in Table 6. Also given are the ^{31}P and ^{195}Pt chemical shifts and the $^{31}P-^{\overline{195}}Pt$ coupling constant for the (Ph₃P)₂Pt complex of ethylene, which serves as a model for the (Ph₃P)₂Pt complex of a planar alkene.²⁶ Although the (Ph₃P)₂Pt complex of bicyclo-[3.3.0]oct-1(5)-ene would have been a better reference for 3a-c, as noted above, we were unable to prepare a stable complex of $(Ph_3P)_2Pt$ with this olefin.

Table 6 shows that, as olefin pyramidalization increases from $(Ph_3P)_2PtC_2H_4$ to **3a**, the ³¹P chemical shift in the (Ph₃P)₂Pt complex moves to higher field. As discussed in the introduction, since olefin pyramidalization lowers the energy of the π^* MO,^{11,12} increased pyramidalization should result in increased back-bonding between the HOMO of $(Ph_3P)_2Pt$ (the antibonding combination of a 5d AO on Pt with the out-of-phase combination of phosphine lone pairs)¹³ and the LUMO

 (π^*) of a coordinated alkene. Ab initio calculations on $(H_3P)_2PtC_2H_4$ confirm that increased pyramidalization does, in fact, result in transfer of electron density from the $(H_3P)_2$ Pt moiety to the olefin.¹⁴ Therefore, one might have expected increased olefin pyramidalization in 3 to result in deshielding of phosphorus and a consequent shift of the ³¹P resonance to lower field. However, just the opposite—an upfield shift of ³¹P with decreasing n—is what is actually observed.

The factors responsible for ³¹P chemical shifts appear not to be entirely understood,³⁷ but there is experimental evidence that transfer of electron density from (Ph₃P)₂Pt to a complexed olefin does, indeed, shift the ³¹P resonances to higher field. It has been found in the $(Ph_3P)_2Pt$ complexes of a series of cyanoethylenes that, as the number of electron-withdrawing cyano groups increases, the ³¹P resonances move upfield.³⁸ Therefore, the upfield ³¹P shifts that are observed in 3, as pyramidalization of the complexed olefin increases, are, in fact, quite consistent with increased electron donation from $(Ph_3P)_2Pt$ to the olefin. Upfield ³¹P shifts have also been reported in (Ph₃P)₂Pt complexes of cyclic acetylenes as bending of the triple bond increases with decreasing ring size.1c

Unlike the ³¹P chemical shifts, the ¹⁹⁵Pt resonances in 3 move to lower field as olefin pyramidalization increases, although the change in ¹⁹⁵Pt chemical shifts is not monotonic.³⁹ Nevertheless, the general trend is consistent not only with the naive expectation that increasing transfer of charge from (Ph₃P)₂Pt to the olefin should deshield Pt but also with the observation that the ¹⁹⁵Pt chemical shifts of (Ph₃P)₂Pt complexes of cyanoethylenes move to lower field as the number of cyano groups increases.38

Table 6 shows that the ³¹P-¹⁹⁵Pt coupling constants in 3 decrease monotonically with the increase in olefin pyramidalization that occurs from 3c to 3a. Interestingly, unlike the trends in ³¹P and ¹⁹⁵Pt chemical shifts, this trend in ³¹P-¹⁹⁵Pt coupling constants is not found in (Ph₃P)₂Pt complexes of cyanoethylenes as the number of cyano groups increases.³⁸ The cyanoethylene complexes show only small variations in the ${}^{31}P-{}^{195}Pt$ coupling constants as the number of cyano groups increases, and the ³¹P-¹⁹⁵Pt coupling constant of the tetracyanoethylene (TCNE) complex is actually 27 Hz larger than that found in the complex of ethylene.

An important factor in the size of ³¹P-¹⁹⁵Pt coupling constants in these complexes is the amount of bonding between the symmetric combination of the lone-pair orbitals on each phosphorus and the empty 6s orbital on platinum.³⁷ The simplest interpretation of the experimental data for 3 and for the $(Ph_3P)_2Pt$ complexes of cyanoethylenes³⁸ is that the bonding between the phosphine lone pairs and the 6s AO on Pt decreases with increasing olefin pyramidalization in 3 but remains

 ⁽³⁷⁾ Pregosin, P. S.; Kunz, R. W. ³¹P and ¹³C NMR of Transition Metal Complexes; Springer-Verlag: New York, 1979.
 (38) Pellizer, G.; Graziani, M.; Lenarda, M.; Heaton, B. T. Polyhe-

dron 1983, 2, 657

⁽³⁹⁾ One possible explanation is that the Pt-C bonding in **3b** is anomalous, because, unlike olefins **2a**,c, **2b** is predicted to have a double bond that is not only pyramidalized but also slightly twisted. Both molecular models and ab initio calculations¹¹ indicate that the two carbon bridge in 2b prefers a geometry in which this molecule has only C_2 rather than C_2 , symmetry. The IR spectrum of the matrix-isolated alkene confirms this prediction.^{16b} The twisting of the twocarbon bridge in 2b is predicted to result in some torsion about the double bond, which is calculated to amount to 3.8°.11 However, the X-ray data (vide supra) do not indicate any more torsion about this C-C bond in 3b than in 3a or 3c.

relatively constant as the number of cyano groups increases in the cyanoethylene complexes.

This interpretation allows one to draw some inferences about bonding between the metal and the olefins in these complexes, since bonding between the phosphine lone pair orbitals and the 6s AO on platinum should decrease as bonding between the filled olefin π MO and the 6s AO increases.^{37,40} Direct experimental evidence for this competition between the phosphine lone pairs and the π MO of the olefin for the 6s AO of platinum comes from the finding that in 3, as the ³¹P-¹⁹⁵Pt coupling constants decrease, there is a linear increase in the ¹³C-¹⁹⁵Pt coupling constants (vide infra).

The decrease in the ${}^{31}P-{}^{195}Pt$ coupling constants with the increase in olefin pyramidalization in 3 thus implies that the interaction between π and 6s increases with increasing pyramidalization. Similarly, the nearly constant value of the ${}^{31}P-{}^{195}Pt$ coupling constant in the cyanoethylenes implies that the interaction between π and 6s remains nearly constant as the number of cyano groups attached to the double bond increases.

Upon superficial consideration, neither of these conclusions seems very reasonable. As noted in the introduction, although pyramidalization of the doubly bonded carbons does raise the energy of the π MO, both calculations¹¹ and experiments¹² find the changes in the π orbital energies to be small. In addition, increasing the number of cyano groups attached to a double bond is, as expected, found not to raise but to lower the energy of the π MO. Applying Koopman's theorem to the photoelectron spectra of ethylene and TCNE shows that four cyano groups lower the energy of the π MO by 1.3 eV.⁴¹

There is a logical resolution of this apparent conflict between what can be inferred about the energies of the π orbitals in **3** and in the (Ph₃P)₂Pt complexes of the cyanoethylenes from the changes in the ³¹P-¹⁹⁵Pt coupling constants and what is known about the energies of the π orbitals in the isolated alkenes. The resolution is simply that the effective energies of the π MOs of the olefins in the complexes are significantly different from the π MO energies of the uncomplexed alkenes.

For this explanation to be correct, the effective energies of the olefin π MOs in **3** would have to increase much faster with increased olefin pyramidalization than is indicated by the rather small changes in the energies of the π orbitals in the isolated alkenes (2). In addition, a similar type of increase in the effective π orbital energies of the cyanoethylenes in their (Ph₃P)₂Pt complexes would be required to approximately cancel the decrease of the energies of the π MOs with increasing numbers of cyano groups in the isolated olefins.

We suggest that the cause of the greater effective π MO energies in the complexed, than in the free alkenes is back-donation from the $(Ph_3P)_2Pt$ HOMO¹³ into π^* . Lowering the energy of π^* , by increasing either the pyramidalization of the olefin or the number of cyano groups attached to the doubly bonded carbons, makes the alkene a better electron acceptor, so that more electron density is transferred from the $(Ph_3P)_2Pt$ HOMO into the olefin LUMO. The transfer of electron

Table 7. ¹³C Chemical Shifts (ppm) of the Olefinic Carbons and ¹J_{C-Pt}, ²J_{C-P}, and ²J_{P-P} Coupling Constants (Hz) for 3a-c and for (Ph₃P)₂PtC₂H₄

complex	ðc	${}^{\mathrm{i}}J_{\mathrm{C-Pt}}$	${}^{2}J_{\rm C-P}^{\rm trans}$	${}^2J_{\mathrm{C-P}}$	$^{2}J_{P-P}$
3a ^a 9ha	66.9 74.0	407	67	-10	-27
30- 3c	74.9 78.8, 79.2 ^b	343 296°	56 48 ^c	-9°	$-41 - 55^{\circ}$
$(Ph_3P)_2PtC_2H_4^a$	39.2	194	27	-3	-58

^a Benzene-d₆, 298 K. ^b Toluene-d₈, 229 K. ^c Toluene-d₈, 338 K.

density into π^* should result in a greater Coulombic energy for the electrons in the π MO and thus raise the effective energy of this orbital.

Increased transfer of charge from the $(Ph_3P)_2Pt$ HOMO into the π^* MO of an olefin thus serves to enhance synergistically electron donation from the π MO of the olefin into empty AOs of the same symmetry on the metal. The consequences of enhanced donation from the olefin π MO into the 6s AO on platinum with increasing olefin pyramidalization in **3** are seen indirectly in the decrease of the ${}^{31}P-{}^{195}Pt$ coupling constants. However, as discussed in the next section, direct evidence for increased donation from π to 6s is provided by the linear increase in the ${}^{13}C-{}^{195}Pt$ coupling constants that accompanies the decrease in the ${}^{31}P-{}^{195}Pt$ coupling constants.

¹³C NMR Spectra of the Complexes. Table 7 gives the ¹³C chemical shifts and the ¹³C-¹⁹⁵Pt and ¹³C-³¹P coupling constants for the olefinic carbons of 3a-c. The ³¹P-³¹P coupling constants, which can be obtained from the ¹³C NMR spectra (*vide infra*), are also given. The ¹³C chemical shifts and all the coupling constants change monotonically with the increase in olefin pyramidalization that accompanies the decrease in n.

Pyramidalization appears to move the ¹³C resonances for olefinic carbons to lower field in uncomplexed alkenes,¹² but the trend for the olefinic carbons of the complexed alkenes in **3** is just the opposite—the ¹³C chemical shifts move toward higher field as pyramidalization increases. We attribute the upfield shifts of these carbons in **3** to increased back-donation of electron density from the (Ph₃P)₂Pt HOMO into the π^* LUMO of the olefin, which increases the diamagnetic shielding of these carbons.

The ¹³C-¹⁹⁵Pt coupling constants for the olefinic carbons increase by 38% on going from n = 3 to n = 1in **3**, and the ¹³C-¹⁹⁵Pt coupling constant for the olefinic carbons in **3a** is more than a factor of 2 larger than that measured in the (Ph₃P)₂Pt complex of ethylene. These ¹³C-¹⁹⁵Pt coupling constants should be roughly proportional to the amount of bonding between the 2s orbital on each carbon and the 6s orbital on platinum.³⁷ The coupling constants will therefore be affected not only by the amount of electron donation from the filled π orbital of each olefin to the 6s orbital of platinum but also by the extent to which the carbon 2s orbitals contribute to bonding to platinum in the complex. Both of these factors are expected to increase with increased pyramidalization of the complexed olefin.

As discussed in the previous section, the observation that the ${}^{31}P-{}^{195}Pt$ coupling constant decreases by 21% on going from the $(Ph_3P)_2Pt$ complex of ethylene to **3a** indicates that bonding between the phosphine lone pairs and the 6s orbital of platinum decreases with increasing olefin pyramidalization. The decrease in the ${}^{31}P-{}^{195}Pt$ coupling constants thus provides good evidence⁴⁰ that

^{(40) (}a) Pidcock, A.; Richards, R. E.; Venanzi, L. M. J. Chem. Soc A 1968, 1707. (b) Allen, F. H.; Pidcock, A. J. Chem. Soc A 1968, 2700.
(c) Church, M. J.; Mays, M. J. J. Chem. Soc A 1968, 3074; 1970, 1938.
(41) Houk, K. N.; Munchausen, L. L. J. Am. Chem. Soc. 1976, 98, 937.

the 110% increase in the ${}^{13}C-{}^{195}Pt$ coupling constant for the olefinic carbons cannot be due solely to an increased contribution of the carbon 2s AOs to carbonplatinum bonding. At least some of the increase in the $^{13}C-^{195}Pt$ coupling constant must be due to increased bonding between the π MO and the 6s AO on platinum.

In fact, a plot of the ³¹P-¹⁹⁵Pt coupling constants in 3a-c, and in the $(Ph_3P)_2Pt$ complex of ethylene, against the ${}^{13}C-{}^{195}Pt$ coupling constants in these complexes gives a good straight line. The equation $J_{P-Pt} = 4460$ $Hz - 3.8J_{C-Pt}$ gives the best least squares fit for the four points with $R^2 = 0.991$. This equation provides evidence that, with increased pyramidalization in 3, the increase in the π -6s bond order results in a linear decrease in the bond order between 6s and the phosphine lone pairs.

For $(Ph_3P)_2Pt$ not coordinated to an alkene, $J_{C-Pt} =$ 0; so the equation predicts $J_{P-Pt} = 4460$ Hz for this species. In fact, this is about the average of the ³¹P-¹⁹⁵Pt coupling constants in bis(phosphine) complexes of Pt(0), which range from 4202 to 4592 Hz.⁴² Perhaps not surprisingly, the equation is less successful when applied to cis-dimethylbis(phosphine)platinum compounds, in which $J_{C-Pt} \approx 600$ Hz.⁴³ The equation predicts $J_{P-Pt} = 2180$ Hz, but the observed ${}^{31}P^{-195}Pt$ coupling constants are somewhat lower, falling in the range 1800-1900 Hz.40b.43

The ³¹P splittings of the resonances for the olefinic carbons in the ¹³C spectra of the (Ph₃P)₂Pt complexes also provide information about the changes in the electronic structure that occur with increasing olefin pyramidalization. The ³¹P nuclei that are *cis* and *trans* to the olefinic carbons in 3 are magnetically nonequivalent. As expected for such an AXX' system, five-line patterns are observed for the olefinic carbons in all the ¹³C spectra, but the appearance of these resonances changes dramatically with increasing pyramidalization of the olefin.

The central portion of the ¹³C spectrum for the olefinic carbons in the $(Ph_3P)_2Pt$ complex of ethylene is a 1:2:1 triplet, flanked by a very weak pair of resonances. The spectrum was simulated using PANIC,⁴⁴ and the values of J_{C-P} of J_{C-P} and J_{P-P} that give the best fit are shown in Table 7. The simulation provides only the relative signs of the coupling constants and does not identify which ${}^{13}C - {}^{31}P$ coupling is J_{C-P} and which is J_{C-P} trans. However, trans coupling constants to phosphines are usually positive and larger in magnitude than cis,³⁷ and use of this additional piece of information allowed the assignments in Table 7 to be made.

As shown in Table 7, in the $(Ph_3P)_2Pt$ complex of ethylene $|J_{P-P}| > |J_{C-P}^{cis} - J_{C-P}^{trans}|$. The much larger magnitude of the coupling of the phosphines to each other than to carbon results in the ¹³C resonances appearing as a 1:2:1 triplet. Only the presence of the very weak pair of resonances that flank this triplet indicate that the phosphines are magnetically nonequivalent and that the peak separations in the triplet are really the average of $J_{\rm C-P}^{\rm cis}$ and $J_{\rm C-P}^{\rm trans.45}$

With increasing pyramidalization, the central resonance decreases in intensity, and the outer pair increase. In 3a, these three peaks have nearly equal intensity, which is roughly 2/3 that of the inner pair of two peaks. The ¹³C spectra for the olefinic carbons in 3a-c were also simulated with PANIC, and the coupling constants in Table 7 were obtained.

As shown in Table 7, as pyramidalization increases. the magnitudes of J_{C-P}^{cis} and J_{C-P}^{trans} increase, while the magnitude of $J_{\rm P-P}$ decreases. As $|J_{\rm C-P}^{\rm cis} - J_{\rm C-P}^{\rm trans}|$ becomes increasingly larger than $|J_{P-P}|$, the ¹³C resonances for the olefinic carbons should eventually become doublets of doublets,⁴⁵ with the two different splittings corresponding to J_{C-P}^{cis} and J_{C-P}^{trans} . Although, even in **3a**, this limit is not reached, the transition from the triplet expected for $|J_{P-P}| \gg |J_{C-P}^{cis} - J_{C-P}^{trans}|$ to the doublet of doublets expected for $|J_{P-P}| \ll |J_{C-P}^{cis} J_{\rm C-P}^{\rm trans}$ is what is being observed in the ¹³C resonances for the olefinic carbons on going from the $(Ph_3P)_2Pt$ complex of ethylene to 3a.

The observed changes in J_{C-P} and J_{P-P} are consistent with the predicted increase in the interaction of the HOMO of a $(R_3P)_2$ Pt fragment with the π^* LUMO of an olefin with increasing pyramidalization.¹⁴ The HOMO of $(R_3P)_2Pt$ consists of the antisymmetric (b_2) combination of phosphorus lone pair orbitals, mixed in an antibonding fashion with $5d_{xz}$ on Pt and in a bonding fashion with $6p_x$.¹³ Therefore, as transfer of electron density from the $(R_3P)_2Pt$ HOMO into π^* of an olefin increases, all the ³¹P coupling constants should be affected.³⁷ The transfer of electron density from phosphorus to carbon should cause the magnitude of J_{P-P} to decrease and the magnitude of both J_{C-P}^{cis} and $J_{\rm C-P}$ ^{trans} to increase. Greater donation from the filled olefin π orbital into the empty 6s and 6p, AOs on the metal with increased olefin pyramidalization may also contribute to the changes in these coupling constants, and the greater contribution of the carbon 2s AOs to both π and π^* is probably responsible for part of the observed increases in the magnitudes of the ${}^{13}C - {}^{31}P$ coupling constants.

Conclusions

The X-ray structures of the $(Ph_3P)_2Pt$ complexes (3) of pyramidalized olefins 2a-c show what the ¹⁹⁵Pt-¹H coupling constants for these complexes in solution suggest-the amount of pyramidalization of the carbons that are bonded to platinum increases substantially from 3c to 3b to 3a. The degree to which these carbons are pyramidalized has a profound effect on the chemical shifts and coupling constants observed in the ³¹P. ¹⁹⁵Pt, and ¹³C NMR spectra of 3a-c. The changes found in these chemical shifts and coupling constants provide confirmatory evidence that a major effect of alkene pyramidalization is to lower the energy of the π^* MO.11.12

Experimental Section

General Methods. Dry deoxygenated diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone. Hexane and pentane, used in flash chromatographic separations, were distilled. Other reagents and solvents were used as obtained, unless otherwise stated.

Flash chromatography was carried out using Silica Gel 60, 40-63 µm (230-400 mesh). Thin-layer chromatography (TLC) was performed on glass supported Silica Gel 60 plates (0.25 mm thick). Gas chromatographic analyses were carried out on a Hewlett-Packard 5790A series gas chromatograph,

⁽⁴²⁾ Mann, B. E.; Musco, A. J. Chem. Soc., Dalton Trans. 1980, 776.
(43) Cheney, A. J.; Mann, B. E.; Shaw, B. L. J. Chem. Soc., Chem. Commun. 1971, 431; Harris, R. K.; McNaught, I. J.; Reams, P.; Packer, K. J. Magn. Reson. Chem. 1991, 29, S60.

⁽⁴⁴⁾ Bruker Instruments, Billerica, MS

⁽⁴⁵⁾ See, for example, ref 32, pp 160-70.

equipped with a 30 m x 0.32 mm i.d., FSOT SE-54, 0.25 μ m, capillary column and coupled to a Hewlett-Packard 3390A integrator.

NMR spectra were obtained on Bruker 200, 300, and 500 MHz instruments. ¹H chemical shifts are reported in ppm downfield from internal TMS, and ¹³C chemical shifts were obtained using CDCl₃ as an internal standard. ³¹P NMR chemical shifts are reported in ppm, relative to 85% H₃PO₄, and (Ph₃P)₂PtC₂H₄ (δ -555)³⁸ served as the standard for ¹⁹⁵Pt chemical shifts.

FAB high-resolution mass spectra were obtained on a VG Analytical 70-SEQ instrument with a 11-250J data system, using a xenon gun. EI spectra were measured either on the same spectrometer or on a medium-resolution Kratos Analytical GCMS with a Mach 3 data system, on a Kratos Analytical GC/MS, on a Hewlett-Packard 5985 GC/MS, or on a Hewlett-Packard 5971A GC/MS.

Infrared absorption spectra were obtained using a Perkin-Elmer 1600 series FTIR and were recorded in solution, versus a solvent reference cell. UV-Vis absorption spectra were measured on a Hewlett-Packard 8452A diode array UV-Vis spectrophotometer.

(Tricyclo[3.3.1.0^{3,7}]non-3(7)-ene)bis(triphenylphosphine)platinum (3a). Diiodide 1a, $X = I_{,15}$ 100 mg (0.27 mmol), and (Ph₃P)₂PtC₂H₄,¹⁹ 200 mg (0.27 mmol), were placed in a flame-dried, nitrogen-purged, two-necked, round-bottom flask. To one neck was attached a dropping funnel containing 8 g of Na/Hg (0.4% Na by weight). The other neck was attached to a vacuum line, the flask was evacuated, and 15 mL of dry THF was distilled in. The flask was then filled with argon and removed from the vacuum line. The sodium amalgam was added in one portion, and the contents of the flask were stirred for 36 h. The reaction mixture was filtered through Celite, and the solids were washed with 20 mL of THF. The THF solutions were combined and evaporated under reduced pressure to give a brown oil. On trituration with ethanol, a beige colored powder was obtained (120 mg, 54%), which was recrystallized from THF-ethanol to give needlelike crystals, mp 192-94 °C, which were pure by NMR. ¹H NMR (500 MHz, C_6D_6): δ 2.06 (s, 2H), 2.20 (d, J = 10.3Hz, 4H), 2.37 (td, $J_{H-Pt} = 52.2$ Hz, $J_{H-H} = 10.3$ Hz, 4H), 3.46 (t, $J_{\text{H-Pt}} = 60.3$ Hz, 2H), 7.12 (m, 18H), 7.22 (m, 12H). ¹³C NMR (75.4 MHz, C₆D₆): δ 138.2, 134.8, 66.9 (t of m, J_{Pt-C} = 407.4 Hz), 61.2 (t, $J_{Pt-C} = 106.7$ Hz), 52.5 (s), 39.3 (s). ³¹P NMR (121 MHz, C₆D₆): δ 30.5 (t of m, $J_{Pt-P} = 2960$ Hz). ¹⁹⁵Pt NMR (42.8 MHz, C₆D₆): δ -467 (t, J_{P-Pt} = 2960 Hz). The FAB mass spectrum showed the parent ion at (M + H)/e = 840 (exact mass: calcd for C45H43P2Pt, m/e 840.2486; found, m/e 840.2497), with peaks at m/e 839 and 841 for the two other abundant isotopes of Pt. Anal. Calcd for $C_{45}H_{42}P_2Pt$: C, 64.35; H, 5.04; P, 7.37. Found: C, 64.39; H, 5.01; P, 7.64.

Acetonide of Tricyclo[3.3.2.03,7]decane-3,7-diol (5). Into a 250 mL round bottom flask, fitted with a condenser, was added 647 mg (2.91 mmol) of ketone 4, 1.42 mL (29.2 mmol) of hydrazine monohydrate, 1.04 g (26.0 mmol) of sodium hydroxide, and 140 mL of diethylene glycol. The mixture was heated at 185 °C under nitrogen for 30 h. The reaction was worked up by cooling to room temperature, adding water, extracting three times with diethyl ether, washing the combined ether extracts twice with water, and drying the ether phase over magnesium sulfate. Diethyl ether was also used to rinse a significant amount of acetonide that had sublimed on the inside wall of the condenser. Solvent removal at reduced pressure on a rotary evaporator gave 629 mg of a solid, which GC and GCMS analysis showed to be 97% acetonide 5 (retention time = 3.28 min at 165 °C). Attempts to recrystallize 5 were unsuccessful. Purification was effected by flash chromatography on 45 g of silica, using diethyl ether-hexane (1:10) as the eluent. This yielded 538 mg (88.7%) of solid white acetonide 5, mp 45.5–46.5 $^{\circ}\mathrm{C},$ in fractions collected when 160– 260 mL of solvent had passed through the column. This material was pure by GC, TLC ($R_f = 0.30$ in 1:10 etherhexane), and NMR. ¹H NMR (CDCl₃, 500 MHz): δ 1.47 (s, 6

H), 1.70 (m, 4 H), 1.88 (d, J = 11.7 Hz, 4 H), 2.16 (dd, J = 11.7 Hz, J = 6.1 Hz, 4 H), 2.39 (m, 2 H). ¹³C NMR (CDCl₃, 50 MHz): δ 29.67 (CH₂), 30.10 (CH₃), 35.50 (CH), 47.66 (CH₂), 98.46 (C), 118.01 (C). IR (CHCl₃, cm⁻¹): 3018, 2943, 2861, 1454, 1372, 1199, 1052. MS (EI): m/e 193 (M⁺ – CH₃, 100), 151 (13.5), 133 (14.6), 109 (15.5), 93 (31.8), 79 (30.3), 67 (28.9), 55 (22.9), 43 (63.2). Exact mass (EI): calcd. for C₁₂H₁₇O₂ (M⁺ – CH₃), m/e 193.1227; found, m/e 193.1220.

Tricyclo[3.3.2.0^{3,7}]decane-3.7-diol (6). A mixture of 49.0 mg (0.236 mmol) of acetonide 5 and 40 mL of 20% aqueous acetic acid was heated at 85 °C for 48 h in a 100 mL round bottom flask, fitted with a condenser. The solution was cooled, and the solvent was removed at reduced pressure on a rotary evaporator. The resulting solid residue was dissolved in 20 mL of chloroform and washed with 20 mL of saturated aqueous sodium bicarbonate. The aqueous phase was extracted with two 20 mL portions of chloroform, and the combined organic phases were dried over magnesium sulfate. Solvent removal at reduced pressure on a rotary evaporator gave 32.9 mg of solid white diol 6 (83.1%), which was pure by GC (retention time = 3.16 min at 165 °C), TLC ($R_f = 0.06$, diethyl etherpentane, 1:1), and NMR. The diol was recrystallized from diethyl ether to give crystals, mp > 260 °C (sublimation begins around 220 °C at 1 atm). ¹H NMR (CDCl₃, 500 MHz): δ 1.68 (m, 4 H), 1.85-1.95 (8 H), 2.10 (m, 2 H), 2.26 (s, 2 H, 30)exchangeable with D_2O). ¹³C NMR (CDCl₃, 50 MHz): δ 29.15 (CH_2) , 29.41 (CH), 48.04 (CH₂), 83.21 (C). IR (CHCl₃, cm⁻¹): 3578, 3402 (broad), 3015, 2936, 2861, 1451, 1322, 1114. MS (EI): $m/e 168 (M^+, 100), 166 (40.8), 150 (9.8), 138 (30.1), 123$ (14.5), 111 (60.6), 109 (63.4), 108 (58.8), 95 (62.0), 81 (61.8), 67 (20.5), 55 (17.8). Exact mass (EI): calcd for $C_{10}H_{16}O_2$, m/e168.1149; found, m/e 168.1144.

 $Tricyclo[3.3.2.0^{3,7}] decane-3,7-diyl Dimesylate (1b, X =$ OMs). To a stirred solution of 37.2 mg (0.221 mmol) of diol 6 in 14 mL of dry THF under argon at 0 °C was added 0.5 mL (0.70 mmol) of a 1.4 M solution of methyllithium in diethyl ether. After 20 min, 0.056 mL (0.724 mmol) of methanesulfonyl chloride was added dropwise. After 3 h, most of the solvent was removed at reduced pressure on a rotary evaporator. To the remaining mixture was added 25 mL water, and the aqueous phase was extracted with 3-25 mL portions of chloroform. The combined organic phases were dried over magnesium sulfate. Solvent removal at reduced pressure on a rotary evaporator gave 59.1 mg of a white solid. Purification by flash chromatography on 7 g of silica, using ethyl acetatehexane, 4:3, as the eluent, gave 37 mg (51.7%) of the dimesylate $(R_f = 0.43$ in ethyl acetate-hexane, 4:3) in fractions collected when 35-45 mL of solvent had passed through the column. Also isolated was 17 mg of monomesylate ($R_f = 0.18$) from fractions collected when 50-100 mL of solvent had passed through the column. Recrystallization of the dimesvlate from chloroform-pentane (1:4) gave clear crystals, mp 134-135 °C, which were pure by NMR. ¹H NMR (CDCl₃, 500 MHz): δ 1.71 (m, 4 H), 2.22 (d, J = 11.8 Hz, 4 H), 2.37 (m, 2 H), 2.60 (dd, J= 11.8 Hz, J = 6.7 Hz, 4 H), 3.09 (s, 6 H). ¹³C NMR (CDCl₃, 50 MHz): δ 28.23 (CH₂), 30.39 (CH), 40.70 (CH₃), 45.70 (CH₂), 96.90 (C). IR (CHCl₃, cm⁻¹): 3025, 2937, 2865, 1343, 1168, 1036, 931, 846. MS (EI): m/e 245 (17.6), 149 (100), 121 (24.0), 109 (33.4), 107 (54.1), 91 (23.3), 79 (32.0). Exact mass (FAB): calcd for $C_{12}H_{21}O_6S_2$, m/e 325.0778; found, m/e 325.0775. Anal. Calcd for C₁₂H₂₀S₂O₆: C, 44.43 ; H, 6.22; S, 19.73. Found: C, 44.42; H, 6.25; S, 19.41.

(Tricyclo[3.3.2.0^{3,7}]dec-3(7)-ene)bis(triphenylphosphine)platinum (3b). A round bottom flask containing dimesylate 1b, X = OMs (201 mg, 0.62 mmol), Na/Hg (prepared by adding 100 mg of Na to 22 g of Hg under inert atmosphere), and $(Ph_3P)_2PtC_2H_4$ (520 mg, 0.70 mmol) was attached to a vacuum line and evacuated. Dry ether (50 ml) was distilled in, the flask was filled with Ar, and the reaction mixture was stirred overnight. Filtration through Celite (under an Ar atmosphere) gave a clear yellow solution. The Celite bed was washed with dry ether (2 × 10 mL). The combined ether solutions were evaporated under vacuum to

Table 8. Crystal, Data Collection, and Refinement Information for X-ray Crystallography of
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	Sa	3b	3c
empirical formula	$C_{45}H_{42}P_2Pt$	$C_{46}H_{44}P_2Pt$	$C_{47}H_{46}P_2Pt$
cryst color and habit	clear rhomb	clear rhomb	clear rhomb
cryst size (mm)	0.1 imes 0.15 imes 0.2	0.25 imes 0.35 imes 0.35	0.2 imes 0.25 imes 0.3
cryst system	orthorhombic	triclinic	triclinic
space group	$P2_{1}2_{1}2_{1}$	PĪ	PĪ
unit cell dimens	a = 9.714(2) Å	a = 11.656(2) Å	a = 11.715(2) Å
	b = 18.533(4) Å	b = 16.548(3) Å	b = 12.015(2) Å
	c = 20.208(4) Å	c = 20.208(4) Å	c = 18.878(3) Å
		$\alpha = 68.37(3)^{\circ}$	$\alpha = 97.76(3)^{\circ}$
		$\beta = 79.33(3)^{\circ}$	$\beta = 109.36(3)^{\circ}$
		$y = 86.70(3)^{\circ}$	$y = 96.90(3)^{\circ}$
Z	4	4	2
abs coeff (mm^{-1})	3.976	3 846	3 756
2θ range (deg)	2.0-50.0	30 - 450	3.0-45.0
index range	$0 \le h \le 12$	0 < h < 11	0 < h < 11
much range	$0 \le k \le 22$	-17 < b < 17	-19 < h < 19
	-4 < l < 24	-29 < l < 99	$-12 \le k \le 12$ -16 < $l < 15$
refleps colled	4439	10 330	$10 \le t \le 10$
independent reflers	$4309 (R_{\odot} = 1.85\%)$	$9814 (R_{\odot} - 1.85\%)$	5007 $5011 (P_1 - 1.490)$
abed reflers $[F > 4.0 \ (\pi F)]$	9954	6951	$3011 (n_{int} - 1.42\%)$
abe corr	somiompirical	comicmpinical	4000
D(D)	0.0975 (0.0949)		o olos (o opps)
I(I(w))	0.0275(0.0242)	0.0200 (0.0208)	0.0195 (0.0235)

afford a yellowish powder, which was washed with pentane $(2 \times 5 \text{ mL})$, ethanol (4 mL), and then recrystallized from THF/ ethanol (1:3) to afford yellowish crystals (220 mg, 42% yield), mp (sealed tube) 185-190 °C (dec), which were pure by NMR. ¹H-NMR (300 MHz, C_6D_6): δ 7.59 (m, 12 H), 6.95 (m, 18 H), 2.97 (bt, 2 H, $J_{\text{H-Pt}} = 39.1 \text{ Hz}$), 2.47 (t of m, 4 H, $J_{\text{H-Pt}} = 69.3$ Hz), 1.83 (m, 8 H). ^{13}C NMR (50.3 MHz, $C_6D_6):\ \delta$ 138.0 (m, C), 134.3 (m, CH), 129.1 (s, CH), 128.0 (s, CH), 74.9 (t of m, $J_{\text{Pt-C}} = 343 \text{ Hz}, \text{ C}), 53.1 (t, J_{\text{Pt-C}} = 105 \text{ Hz}, \text{ CH}), 48.4 (t, J_{\text{Pt-C}})$ = 24 Hz, CH₂), 31.6 (s, CH₂). ³¹P NMR (81 MHz, C₆D₆): δ 31.1 (t of m, $J_{P-Pt} = 3115$ Hz). ¹⁹⁵Pt NMR (42.8 MHz, C₆D₆): δ -514 (t, $J_{\rm P-Pt}$ = 3115 Hz). The FAB mass spectrum showed the parent ion at (M + H)/e = 854 (exact mass: calcd for $C_{46}H_{45}P_2Pt$, m/e 854.2644; found, m/e 854.2598), with peaks at m/e 853 and 855 for the two other abundant isotopes of Pt. Anal. Calcd for C₄₆H₄₄P₂Pt: C, 64.71; H, 5.19; P, 7.25. Found: C, 64.71; H, 5.11; P, 7.56.

(Tricyclo[3.3.3.0^{3,7}]undec-3(7)-ene)bis(triphenylphosphine)platinum (3c). A round bottom flask containing dimesylate 1c, X = OMs¹¹ (212 mg, 0.63 mmol) and Na/Hg (prepared by adding 100 mg of Na to 22 g of Hg under inert atmosphere) was attached to a vacuum line and evacuated. Dry ether (40 mL) was distilled in, the flask was filled with Ar, and the reaction mixture was stirred overnight. The reaction mixture was concentrated to about half its volume by bubbling Ar through it, and then it was filtered through Celite (under Ar atmosphere) into a solution of (Ph₃P)₂PtC₂H₄ (420 mg, 0.56 mmol) in dry THF (30 mL). Removal of the solvent under vacuum afforded a yellowish powder which was recrystallized from THF/ethanol (1:3) to give yellowish crystals (235 mg, 43% yield based on the (Ph₃P)₂Pt complex of ethylene), mp (sealed tube) 145-148 °C (dec), which were pure by NMR. ¹H-NMR (500 MHz, toluene-d₈, 245 K): δ 7.54 (m, 12 H), 6.96 (m, 18 H), 2.88 (t of m, 2 H, $J_{H-Pt} = 80.6$ Hz), 2.80 (m, 2 H), 2.54 (t of m, 2 H, $J_{\rm H-Pt}$ = 80.6 Hz), 2.36 (t of d, 2H, $J_{\rm H-Pt}$ = 20.1 Hz, J_{H-H} = 13.7 Hz), 2.10 (t of d, 2H, J_{H-Pt} = 20.1 Hz, $J_{\rm H-H} = 14.0$ Hz), 1.98 (bm, 3 H), 1.67 (m, 1 H), 1.52 (t, 2H, J = 13.5 Hz). ¹H-NMR (500 MHz, C₆D₆, 338 K): δ 7.58 (m, 12 H), 6.98 (m, 18 H), 2.71 (bm, 2 H), 2.64 (bt, 4 H, $J_{H-Pt} = 80$ Hz), 2.14 (bd, 4 H, $J_{H-Pt} = 20.1$ Hz), 1.75–1.69 (b, 6 H). ¹³C NMR (50.3 MHz, toluene-d₈, 229 K): δ 138.3 (m, C), 134.2 (m, CH), 129.0 (s, CH), 128.0 (s, CH), 79.2 (m, C), 78.8 (m, C), 52.2 (t, $J_{Pt-C} = 32$ Hz, CH₂), 50.7 (t, $J_{Pt-C} = 76$ Hz, CH), 41.5 (t, $J_{\text{Pt-C}} = 32$ Hz, CH₂), 36.9 (s, CH₂), 23.1 (s, CH₂). ¹³C NMR (50.3 MHz, toluene- d_8 , 338 K): δ 138.6 (m, C), 134.4 (b, CH), 129.0 (s, CH), 128.0 (s, CH), 79.2 (t of m, $J_{Pt-C} = 296$ Hz, C), 50.8 (t, $J_{Pt-C} = 76$ Hz, CH), 47.4 (b, CH₂), 36.9 (s, CH₂), 23.1 (s, CH₂). ³¹P NMR (81 MHz, C₆D₆): δ 32.2 (t of m, $J_{P-Pt} =$ 3332 Hz);¹⁹⁵Pt NMR (toluene- d_8 , 42.8 MHz): δ -501 (t, $J_{P-Pt} =$ 3332 Hz). The FAB mass spectrum showed the parent ion at M⁺/e = 867 (exact mass: calculated for C₄₇H₄₆P₂Pt, *m*/e 867.2646, found *m*/e 867.2630), with peaks at *m*/e 866 and 868 for the two other abundant isotopes of Pt. Anal. Calcd for C₄₇H₄₆P₂Pt: C, 65.04; H, 5.34; P, 7.14. Found: C, 64.85; H, 5.21; P, 7.15.

X-ray Structures of (Tricyclo[3.3.1.0^{3,7}]non-3(7)-ene)bis(triphenyl-phosphine)platinum (3a),¹⁸ (Tricyclo-[3.3.2.0^{3,7}]dec-3(7)-ene)bis(tri-phenylphosphine)platinum (3b), and (Tricyclo-[3.3.3.0^{3,7}]undec-3(7)-ene)bis-(triphenylphosphine)platinum (3c). Suitable crystals of all three complexes were chosen and mounted with grease in capillaries, which were sealed with a torch. Descriptions of the crystals and the X-ray data collection are contained in Table 8. Reflections were collected for the three crystals, using an Enraf-Nonius CAD4 diffractometer with Mo Ka radiation $(\lambda = 0.710~73$ Å) and a highly oriented graphite crystal monochromator. Data reduction was performed using the program XCAD4, followed by Siemen's SHELX XEMP for making absorption corrections, based on ψ -scan data. Structures were solved using direct and Fourier transform methods. Solutions and subsequent refinements were carried out using the PC version of SHELX. The Laue merging R factors for equivalent reflections were good, and densities agreed with the space groups found. The crystal of 3b gave two independent molecules per unit cell in $P\overline{1}$. This result was examined carefully, but no higher space group was possible for the observed intensities. Additional information about the X-ray structure determinations is available as supporting information.24

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Supporting Information Available: Tables of bond lengths, bond angles, anisotropic displacement coefficients, and hydrogen atom coordinates and U values for 3a-c (15 pages). Ordering information is given on any current masthead page.

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