Synthesis of 1,3-Divinylcyclopentane Derivatives from Platina(IV)cyclobutane Complexes

F. F. Stewart, W. D. Neilsen, R. E. Ekeland, R. D. Larsen, and P. W. Jennings*

Gaines Hall, Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59717-0340

Received April 30, 1993®

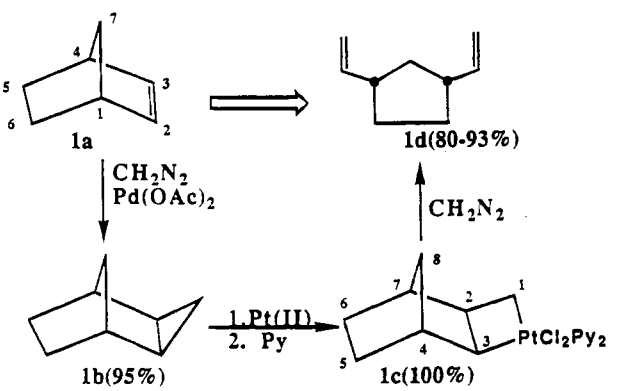
A new transformation is reported in which a norbornyl-substituted platina(IV)cyclobutane complex is reacted with selected diazo derivatives to yield *cis*-1,3-divinylcyclopentane products in excellent yields. The distal substituent on one vinyl moiety is formed stereospecifically, while the substituent on the other vinyl moiety is not. Mechanistic details suggest a specific binding site for the diazo derivative leading to formation of a metallacyclopentane intermediate which spontaneously yields the divinyl product. The first crystal structure of a platina(IV)-cyclobutane bearing an electron-withdrawing aldehyde functionality is also included.

Recent efforts in this laboratory have been concentrated on the discovery of new organic transformations which are facilitated by platinum.[1] In this article, we wish to describe the stereochemical results and some mechanistic insight on the transformation shown in Scheme I.[2] Since the steps for this transformation were quite facile as indicated, it was decided that further stereochemical elaboration might prove to be useful for future synthetic strategies. In addition, strategic substitutions on the system might yield evidence on the mechanism of the last step, which is further elaborated in Scheme II.

Parallel pathways are shown in Scheme II, with path A being favored because it leads to the product. Path B is included for comparison as well as to more easily show that it is not viable. Three aspects of Scheme II are of particular importance and deserve further discussion. First, due to the trans effect of the carbons in the cyclobutane ring, the pyridine ligands are readily lost. Presumably during one of these vacancies the diazo derivative coordinates. Obviously there are two sites, **2a** and **2a′**. Additional evidence with regard to the fact that a vacant site is necessary is that (a) the pyridine ligands exchange very rapidly with perdeuteriopyridine in $CDCl_3$, as determined by NMR spectroscopy, and (b) the reaction **1c** → **2d** does not proceed if the bipyridine analog of **1c** is used.

Second intermediate **2c*** is proposed as (a) it logically leads to the product through a 2 + 2 + 2 cycloreversion process, (b) its decomposition would yield a negative enthalpy from loss of norbornyl ring strain energy, and (c) the unsymmetrical platinacyclopentane **2c′** which would be derived from an alternative coordination and bond migration (path B) does not lead to the observed product. Further, we have synthesized **2c′** by a different route and it is quite stable under these reaction conditions.[3] Thus, we believe that **2d*** is formed by pyridine dissociation

Scheme I



followed by coordination of the diazomethane at the position shown in structure **2b*** with subsequent ring expansion to yield the symmetrical metallacycle, which decomposes spontaneously. Finally, the formation of **2b** by carbon coordination rather than nitrogen coordination is conjecture. However, in recent articles, evidence was given for carbon coordination in diazo derivatives.[4]

Additional Stereochemistry

The first query with regard to additional stereochemistry in this reaction involved the direct substitution on the cyclopropane moiety, which subsequently translates to stereochemical consequences at one of the vinylogous termini. If the stereochemistry is controlled from the cyclopropane derivative to the divinyl product, it would lend credence to the sequence shown in Scheme II as path A. The reaction sequence shown as Scheme III exhibits the details of substrate synthesis for this portion of the investigation: It was necessary to reduce the esters resulting from the cyclopropanation step, as platinum(II) in the form of Zeise's dimer will not insert into a cyclopropane bearing an electron-withdrawing functionality.[5] In the oxidative-addition step, if the concentration of Pt(II) is limited to the concentration of **3a**, one effects a clean kinetic separation of epimers, as **3a** reacts with

* Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) (a) Stewart, F. F.; Jennings, P. W. *J. Am. Chem. Soc.* **1991**, *113*, 7037. (b) Hoberg, J. O.; Larsen, R. D.; Jennings, P. W. *Organometallics* **1990**, *9*, 1334. (c) Hiscox, W.; Jennings, P. W. *Organometallics* **1990**, *9*, 1997.

(2) A preliminary report of this work has been published as a communication: Neilsen, W. D.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* **1988**, *110*, 3307.

(3) Stewart, F. F. Ph.D. Thesis, Montana State University, 1992. Neilsen, W. D.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* **1988**, *110*, 8657.

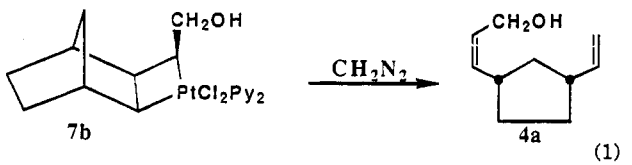
(4) (a) Maxwell, J. L.; Brown, K. C.; Bartley, D. W.; Kodadek, T. *Science* **1992**, *256*, 1544. (b) Doyle, M. P. *Chem. Rev.* **1988**, *86*, 919. (c) Chang, S. C.; Hauge, R. H.; Kafafi, Z. H.; Margrave, J. L.; Billups, W. E. *J. Am. Chem. Soc.* **1988**, *110*, 7975.

0276-7333/93/2312-4585$04.00/0

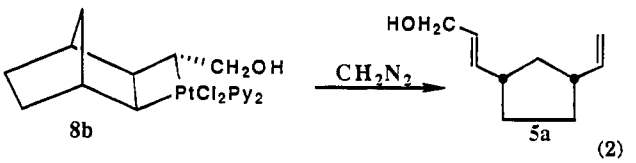
Pt(II) at a rate ~2 orders of magnitude faster than **3b**.[6] Since the reaction with Pt(II) yields the platina(IV)-cyclobutane as a precipitate, one merely filters the solution to separate **3b** from **7a**. Subsequent treatment of the precipitate **7a** with pyridine yields **7b**. Reaction of **3b** for a longer period of time with Pt(II) yields **8a**, and the addition of pyridine gives **8b**.

Complexes **7b** and **8b** represent the first reported examples of 2,3,4-trisubstituted platina(IV)cyclobutanes.[2] Moreover, it is significant that the syn isomer (**3a**) is faster in its reaction with Pt(II) than the anti epimer **3b**. Two reasons are postulated for the rate difference: (a) edge attack by the Pt(II) moiety has fewer degrees of freedom in the anti case due to steric constraints, and (b) the energy of **3a** is greater than that of **3b** by about 3 kcal[7] due to the bridge CH_2–cyclopropyl CH_2OH interaction.

When complexes **7b** and **8b** were separated and completely characterized by NMR spectroscopy and X-ray crystallography,[2] they were subjected to reaction with diazomethane. The results are shown in eqs 1 and 2. There



(1)



(2)

was no evidence via NMR spectroscopy in the crude reaction mixtures for the presence of compound **5a** in the product of equation 1 and vice versa. Thus, it is apparent that the diazo reaction is stereospecific in the formation of compounds **4a** and **5a** with regard to the olefin and the substituents on the cyclopentane ring. This is consistent with the concerted 2 + 2 + 2 retro-cycloaddition mechanistic sequence proposed in Scheme II. Moreover, it is important to note that this process, by virtue of the reaction and the bicyclic character of the substrate, yields products which have two stereo centers and one olefinic site of stereochemistry unambiguously predetermined.

Given that other positions on the original norbornyl system could be stereochemically established prior to the reaction sequence, it became apparent that several, if not all, of the carbon atoms might be stereochemically controlled in this reaction. For example, spectator groups on carbons 5 and 6 in **1a** could be established prior to

Scheme II

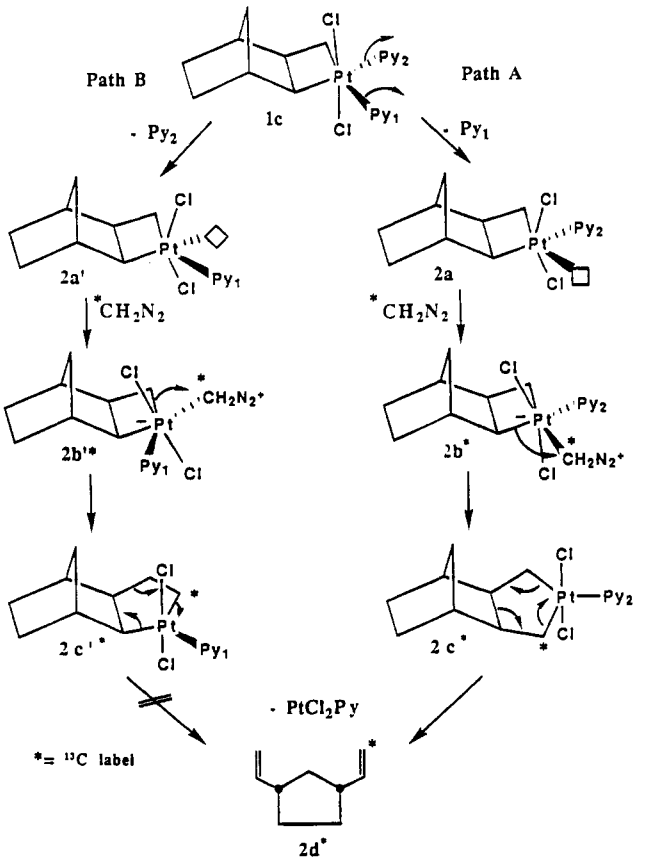


Table I. Reactants and Products from the Divinylation Process

Pt compd	reactant G	*E*/*Z* product ratio	product
6	H	1.4 ± 0.2	**13**
7	CH_2OH (syn)	*0.7 ± 0.2*	**14**
8	CH_2OH (anti)	1.5 ± 0.2	**15**
9	Me (syn)	1.5 ± 0.2	**16**
10	CHO (syn)	1.6 ± 0.2	**17**
11	CHO (anti)	1.4 ± 0.2	**18**
12	CH_2OMe (syn)	*1.7 ± 0.2*	**19**

reaction and should, in principle, be carried through the reaction sequence without isomerization.[2,8]

The next query dealt with the stereochemistry about the other vinyl terminus which is derived from the diazo reagent. In order to address this question, an unsymmetrical diazo derivative (ethyl diazoacetate, EDA) was employed with a variety of norbornyl platina(IV)cyclobutane complexes as shown in eq 3. As expected, the

(3)

G= H(6); CH_2OH(syn=7, anti=8); CH_3(syn=9); CHO(syn=10, anti=11), CH_2OMe(syn=12)

stereochemical consequence of the vinyl moiety bearing G was unaffected by the reaction (i.e., syn → *Z* and anti → *E*) in accord with eqs 1 and 2. Table I contains a list of substrates with the product ratio *E*/*Z* referring to the

(5) (a) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149. (b) Moats, R. Ph.D. Thesis, Montana State University, 1990. Unpublished results show that an ester is tolerable if an olefin is conjugated with the cyclopropyl moiety.

(6) There is some confusion over the relative reactivities of *cis*- and *trans*-cyclopropane isomers. McQuillin (*Tetrahedron Lett.* **1971**, *36*, 3313) had suggested that only the trans-disubstituted cyclopropanes formed platina(V)cyclobutanes. What was inferred from this statement was that the cis isomers did not react. In fact, what appears to happen is that the cis isomer makes the metallacyclobutane and proceeds to react further. Our results clearly indicate that the cis isomer reacts faster than the trans isomer to form the cyclobutane complex.

(7) A value of 2.7 kcal/mol for the energy difference between **3a** and **3b** was calculated using MM2: Moats, R. Ph.D. Thesis, Montana State University, 1990, and unpublished results.

(8) Ekeland, R. A.; Jennings, P. W. *J. Organomet. Chem.* **1985**, *281*, 397.

Scheme III

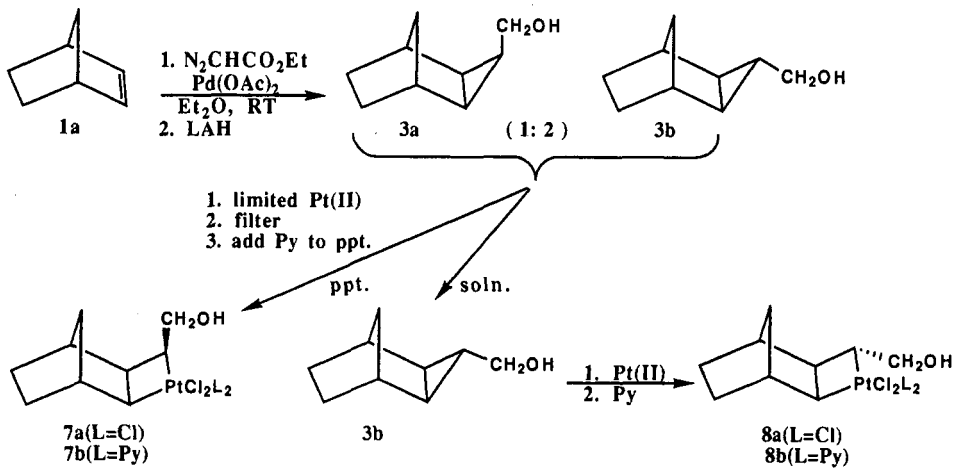
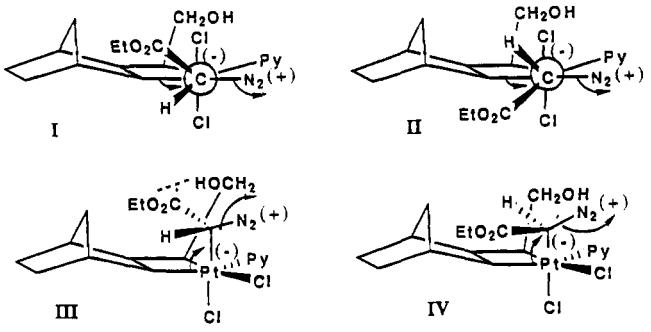


Chart I



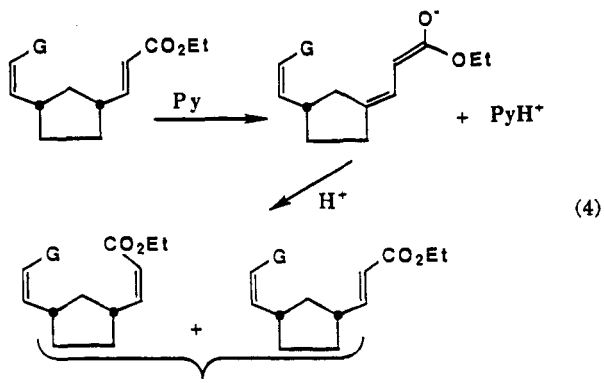
stereochemistry of the vinyl moiety derived from the EDA reaction with the platina(IV)cyclobutane, as shown in eq 3.

It is clear from these results that there is slight stereoselectivity observed at the second vinyl terminus. Among this group of substrates, however, the syn hydroxymethyl substituent stands alone in having an inverse influence on the alkene stereochemistry. As a probe for the basis of this influence, the last entry was proposed, prepared, and reacted. As can be seen, masking of the hydroxyl hydrogen results in the "normal" influence. Thus, it was concluded that some type of hydrogen-bonding interaction occurs between the *syn*-CH_2OH and the N_2-$CHCO_2Et$ moiety. To rationalize these results, four structures are proposed as intermediates (I–IV; Chart I).

Intermediates I and III yield the *Z* isomer, while II and IV lead to the *E* isomer. Of these, only III has the potential for hydrogen bonding to the hydroxymethyl group. Steric crowding and the fact that an eight-membered ring would be required for hydrogen bonding to occur does not bode well for this idea. However, an alternative and perhaps more viable suggestion is that the hydrogen-bonding interaction occurs prior to complexation of the diazo derivative with platinum. Assuming this is true, why do we not observe a higher *Z* component in the ratio? To rationalize the observed results, we suggest that intermediates I and II are responsible for 63% of the reaction, giving a "normal" *E*/*Z* ratio of 1.6. The remaining 37% of the product, however, is proposed to be derived entirely from intermediate III. This argument, if true, would exclude intermediate IV, which the authors believe is reasonable. Finally, the minor significance of intermediate III relative to intermediates I and II is rationalized on the basis that III is in a sterically encumbered system.

Since all of the remaining syn or anti substituents exhibit nearly the same influence as hydrogen, intermediates I and II are suggested for their results. Further, since the *anti*-hydroxymethyl substituent shows no "hydrogen-bonding" influence, the Cl ligand under the ring system is excluded as a site of diazo coordination and thereby lends support for intermediate III. If intermediates I and II are correct, the question arises as to why the asymmetry of the norbornyl portion does not influence the product stereochemistry to a larger extent. Our explanation is that the platinum–carbon distance of the diazo derivative is approximately 2 Å, which is quite long.[9] In carbon systems from which basic reasoning of gauche interactions is often derived, the carbon–carbon bond distance would be only 1.5 Å. Thus, the influence of the norbornyl ring is thought to be lessened in the platinum derivative. Further, the platinum atom is bent down out of the carbon plane, lessening the asymmetrical interaction.

One possible flaw in these arguments is that the observed isomer may be derived from a base-catalyzed isomerization of the olefin, as shown in equation 4.[10]



(4)

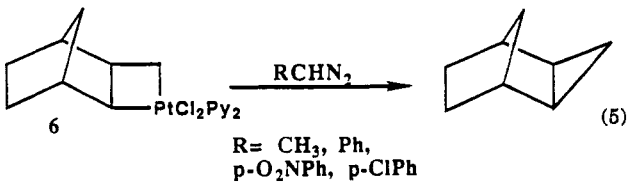
Assistance could also be garnered from a species in which platinum is participating as a Lewis acid. However, refluxing of the syn hydroxymethyl products and the other isomeric products from 12 in the reaction medium failed to change the isomeric ratios.

Additional evidence was subsequently sought to further substantiate the "syn hydroxymethyl effect" and to *further*

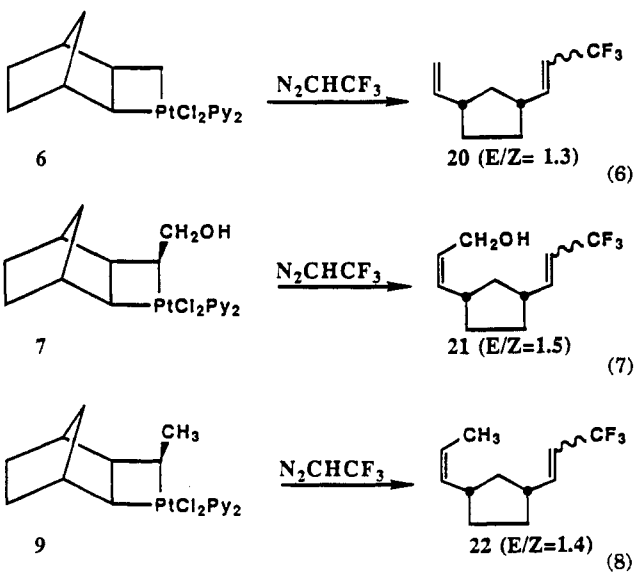
(9) The typical Pt^{IV}–C distance in several of our structures is 2.07–2.13 Å.

(10) Thanks to Professor Robert Bergman, Berkeley, CA, for suggesting this query.

broaden the scope of this reaction. In this endeavor a few other unsymmetrical diazo derivatives were investigated (eq 5).



As can be seen, all resulted in reductive elimination with no divinylcyclopentane product detected via NMR spectroscopy. While it is not entirely clear why these reagents fail to produce the divinyl product, we suggest that they are too electron donating as compared to diazoacetic ester, which yields no cyclopropane product. This follows, since it is known that nucleophilic ligands such as tertiary phosphines readily result in the reductive elimination of cyclopropanated products. Thus, it is suggested that the "correct" electron density at the carbon of the diazo reagent is required. With this idea in mind, 2,2,2-trifluorodiazoethane, which should be less basic than those reagents shown in equation 5, was employed (eq 6). Measurement



of the cis/trans ratio of products from eq 6 by proton NMR spectroscopy at 500 MHz gave the "normal" E/Z value of 1.3. It is intriguing to note that $^4J_{H,F}$ was pronounced in the E isomer only, presumably via spatial juxtaposition.[11] Subsequent reaction of this reagent with the *syn*-hydroxymethyl and the *syn*-methyl complexes (eqs 7 and 8) resulted in the formation of both isomers with the "normal" $E/Z = 1.5 \pm 0.2$ in each case. These data clearly corroborate the earlier results and support the hypotheses that (a) there is an association in the reaction between the hydroxy group in **7a** and diazoacetic ester reagent and (b) there is an electron density requirement in the diazo reagent which is necessary to facilitate the production of divinylcyclopentanes.

X-ray Analysis of Complex 11

Complex **11** represents one of the few platina(IV)-cyclobutanes having an electron-withdrawing functionality.[12] Thus, during characterization, it was decided to employ single-crystal X-ray analysis in addition to NMR spectroscopy. It was prepared by PDC oxidation of **8** and crystallized in a chamber containing chloroform and heptane as solvents. A thermal ellipsoid drawing is shown in Figure 1 and represents the first X-ray structure of a platina(IV)cyclobutane bearing an electron-withdrawing functionality. Selected bond distances and angles for **11** are listed in Table II and compared to those from the structure of the hydroxymethyl analog **8**.[2] Except for a slight difference in the pucker of the metallacyclobutane ring, which is expected, these two structures compare incredibly well, indicating that the carbonyl group has little influence on the structural characteristics of the ring. Atomic coordinates are listed in Table III.

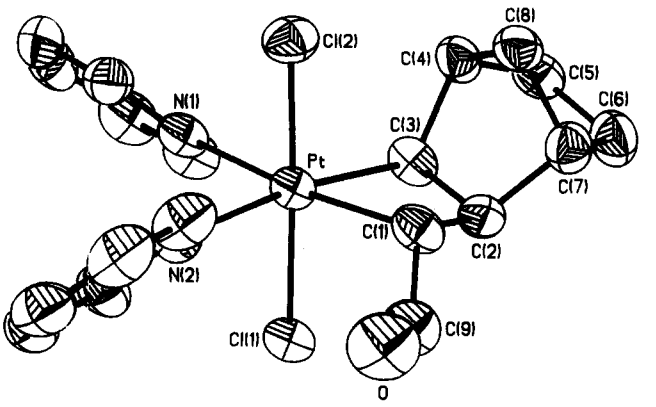


Figure 1. Thermal ellipsoid (50% probability) drawing of complex **11** with labeling scheme.

Table II. Selected Bond Distances (Å) and Angles (deg) for Complexes 11 and 8

	11	8
Pt–Cl(1)	2.335(2)	2.335(2)
Pt–Cl(2)	2.314(2)	2.314(2)
Pt–C(1)	2.07(1)	2.071(10)
Pt–C(3)	2.07(1)	2.074(8)
Pt–N(1)	2.189(7)	2.189(7)
Pt–N(2)	2.238(7)	2.238(7)
Cl(1)–Pt–Cl(2)	178.0(1)	178.0(1)
C(1)–Pt–C(3)	68.7(3)	68.7(3)
N(1)–Pt–N(2)	90.2(3)	90.2(3)
metallacyclobutane pucker angle	15	17

Summary

A sequence of reactions beginning with norbornenyl derivatives and facilitated by Pt(II) has been elaborated in a one-step metathesis type methodology to yield *cis*-1,3-divinylcyclopentane derivatives in good yield. The terminal stereochemistry at one of the vinylic arms is formed stereospecifically and is predetermined by the stereochemistry of the substrate. At the terminus of the second vinylic moiety derived from reaction of the platinacycle and an unsymmetrical diazo derivative, the olefin is not formed stereospecifically. In general, at this terminus, there is a slight preference for the E isomer, except in the case where hydrogen bonding can influence the product stereochemistry. While the hydrogen-bonding pathway appears to yield stereospecific products, unfortunately it is not the major pathway.

(11) Hughes, R. P. Personal communication, Dartmouth University.

(12) Hoberg, J. O.; Jennings, P. W. *Organometallics* **1991**, *10*, 8. A methodology for the synthesis of platina(IV)cyclobutanes with electron-withdrawing groups has been achieved with further conclusions that they are quite stable. Thus, their direct formation is a kinetic problem.

Table III. Positional Coordinates and Isotropic Thermal Parameters (Å²) with Standard Deviations in Parentheses for $C_{19}H_{22}N_2OCl_2Pt\cdot CHCl_3$

	x/a	y/b	z/c	U[a]
Pt	0.22938(4)	0.20656(3)	0.21040(3)	0.0357(1)
Cl(1)	0.1472(2)	0.2032(2)	0.4060(2)	0.047(1)
Cl(2)	0.3184(3)	0.2086(2)	0.0187(2)	0.056(1)
C(1)	0.110(1)	0.058(1)	0.201(1)	0.048(3)
C(2)	0.027(1)	0.136(1)	0.193(1)	0.045(3)
C(3)	0.029(1)	0.267(1)	0.170(1)	0.041(3)
C(4)	0.011(1)	0.317(8)	0.042(1)	0.048(3)
C(5)	0.165(1)	0.356(1)	0.059(1)	0.052(3)
C(6)	0.237(1)	0.230(1)	0.093(1)	0.056(4)
C(7)	0.115(1)	0.133(1)	0.087(1)	0.050(3)
C(8)	0.022(1)	0.198(1)	0.014(1)	0.052(3)
C(9)	0.124(1)	0.042(1)	0.302(1)	0.060(4)
O	0.208(1)	0.129(1)	0.308(1)	0.084(4)
N(1)	0.312(1)	0.389(1)	0.210(1)	0.043(2)
C(10)	0.439(1)	0.417(1)	0.162(1)	0.050(3)
C(11)	0.490(1)	0.534(1)	0.155(1)	0.059(4)
C(12)	0.408(1)	0.624(1)	0.202(1)	0.063(4)
C(13)	0.278(1)	0.595(1)	0.252(1)	0.057(4)
C(14)	0.235(1)	0.477(1)	0.256(1)	0.050(3)
N(2)	0.430(1)	0.113(1)	0.271(1)	0.047(3)
C(15)	0.489(1)	0.017(1)	0.223(1)	0.065(4)
C(16)	0.603(1)	0.048(1)	0.262(1)	0.074(5)
C(17)	0.668(1)	0.014(1)	0.354(1)	0.074(5)
C(18)	0.612(1)	0.087(1)	0.406(1)	0.077(5)
C(19)	0.489(1)	0.148(1)	0.362(1)	0.060(4)
C(20)	0.201(1)	0.422(1)	0.589(1)	0.069(4)
Cl(3)	0.3764(4)	0.3989(5)	0.5648(4)	0.107(2)
Cl(4)	0.1449(5)	0.5801(4)	0.5676(4)	0.117(2)
Cl(5)	0.1434(5)	0.3514(4)	0.7250(4)	0.124(2)

[a] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

It appears that diazo derivatives which are somewhat electron deficient are required for successful formation of the divinyl product as opposed to the formation of reductive-elimination products which result from electron-rich diazo reagents. A reaction pathway is proposed wherein the diazo derivative coordinates to the platinum(IV) of the cyclobutane, which subsequently ring-expands to form a symmetrical platina(IV)cyclopentane that decomposes to release norbornyl ring strain and yields the divinylcyclopentane derivatives. Finally, the first X-ray crystal structure is presented for a platina(IV)-cyclobutane complex bearing an electron-withdrawing aldehydic functionality.

Experimental Section

General Considerations. Norbornene, ethyl diazoacetate, and lithium aluminum hydride were obtained from Aldrich and used without purification. Diethyl ether and tetrahydrofuran, purchased from Fisher, were freshly distilled from sodium and benzophenone prior to use. NMR spectra were obtained using Bruker Models WM250 (^{1}H, 250 MHz), AC300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz), and AM500 (^{1}H, 500 MHz; ^{13}C, 125 MHz). Absolute masses were acquired using a VG 7070 mass spectrometer.

Synthesis of Hydrocarbon 1b. Hydrocarbon **1b** was synthesized by the method of Kottwitz[13] with the following modification. The ethereal solution containing the product was rotavaporated to remove the ether and the residue was chromatographed on silica using pentane as the eluent.

Reaction of 1b with Platinum(II). In a 25-mL flask containing 56 mg (0.51 mmol) of **1b** and 10 mL of diethyl ether, 0.15 g (1 equiv, 0.26 mmol) of Ziese's dimer was added and the resulting mixture stirred at reflux for 6 h. Subsequently, the volume of solvent was reduced to 1 mL and the concentrate was triturated three times with pentane to give a yellow solid residue. It was dried and treated with 10 mL of diethyl ether and 2 equiv of pyridine. This solution was stirred at room temperature for 15 min, upon which it was reduced to a volume of 1 mL and triturated three times with pentane to remove excess pyridine. The residue, complex **6(1c)**, was then dried under N_2. This complex has been previously reported.

Synthesis of 3a and 3b. To 10 g (0.11 mol) of norbornene in 50 mL of diethyl ether was added 17 mL (0.17 mol) of ethyl diazoacetate in 75 mL of diethyl ether in the presence of rhodium(II) acetate. This mixture was stirred for 12 h. After removal of the ether by rotavaporation, 18.2 g (95% yield) of the yellow liquid epimeric esters was obtained. They were subsequently chromatographed on silica gel using benzene as the eluent. The resultant yellow oil was added dropwise to a slurry of LAH (15 g) in 100 mL of diethyl ether at 0 °C. After 12 h, the reaction was quenched using acidic deionized water added dropwise and the product was extracted using diethyl ether. These washings were collected and washed with three 50-mL portions of water. Rotavaporation and subsequent vacuum distillation (73 °C at 8 mmHg) of the organic phase gave 8.8 g of epimeric alcohols **3a** and **3b** (63% yield; anti to syn ratio 2.2). These are known compounds.[3]

Synthesis of 7a and 7b. To 0.23 g (1.63 mmol) of the epimeric alcohol mixture in a 50-mL round-bottom flask was added 20 mL of diethyl ether and 1 equiv (0.15 g, 0.25 mmol), equal to the amount of the syn isomer, of Zeise's dimer. The solution was stirred for 2 h at room temperature to ensure complete reaction. All but 1 mL of the solvent was then removed, followed by trituration of the precipitate using three 20-mL portions of pentane. The pentane washings were collected to yield pure **3b**. The remaining precipitate, **7a**, was dried under a stream of dry N_2 **7a**). To this precipitate was added 20 mL of diethyl ether and 2 equiv of pyridine. The solution was stirred at room temperature for 30 min, followed by trituration with pentane, yielding a yellow solid, **7b** (0.27 g, 93% yield). These complexes are known.[3]

Reaction of Platinum Complexes 7b and 8b with Diazomethane. To a solution of platinum complex **7b** or **8b** (0.100 g, 0.178 mmol) in $CDCl_3$ (5 mL) was bubbled diazomethane generated from a 10-fold excess of Diazald (0.287 g, 1.78 mmol). Upon completion of the addition the color of the solution had deepened and the reaction mixture was stirred for 20 min. Compound **4a** was analyzed by NMR and mass spectrometry: *m/e* 152 (M^+); ^{1}H NMR ($CDCl_3$; ppm): 5.78 (m, 1H), 5.49 (overlapping m, 2H), 4.95 (dd, 1H), 4.88 (dd, 1H), 4.21 (d, 2H), 2.81 (m, 1H), 2.52 (m, 1H), 2.0–1.2 (overlapping m, 6H). Compound **5a** was analyzed by NMR and mass spectrometry: *m/e* 152 (M^+); ^{1}H NMR ($CDCl_3$; ppm): 5.76 (dt, 1H), 5.64 (overlapping m, 2H), 4.95 (dd, 1H), 4.88 (dd, 1H), 4.08 (d, 2H), 2.81 (m, 1H), 2.52 (m, 1H), 2.0–1.2 (overlapping m, 6H).

Synthesis of 8. To a solution of 0.07 g (0.51 mmol) of **3b** in 20 mL of diethyl ether was added 0.15 g (0.25 mmol) of Zeise's dimer, and the resulting solution was stirred at room temperature for 6 h to ensure complete reaction. This reaction mixture was treated in the same manner as **7a** to give 0.26 g of **8b** (92% yield).

Synthesis of *syn*- and *anti*-9. Seven milliliters of water and 6.9 g (0.123 mmol) of KOH were placed in a 250-mL round-bottom flask and cooled in an ice bath. To this was added 77 mL of diethyl ether, and the mixture was stirred for 10 min followed by the addition of 3.0 g (0.019 mmol) of 1-ethyl-3-nitro-1-guanidine over 15 min. Upon completion of the addition, the ether layer was added to another flask containing 1.5 g (0.016 mmol) of norbornene and a catalytic amount of palladium(II) acetate. The mixture was stirred in an ice bath for 12 h. The aqueous KOH layer was then washed with diethyl ether three times, and these washings were added to the norbornene solution, which was warmed to room temperature with stirring over 4 h, filtered, and rotavaporated. Subsequently the product was chromatographed on silica gel using pentane as the eluent. The combined fractions were rotavaporated, resulting in 3.4 g (65% yield) of a colorless oil, *syn*- and *anti*-methylcyclopropyl derivatives (anti/syn 1.35). ^{1}H NMR ($CDCl_3$; ppm): 2.42 (br s, 2H),

(13) Kottwitz, J.; Vorbruggen, H. *Synthesis* **1975**, 636.

2.32 (br s, 2H), 2.19 (br s, 4H), 1.38 (m, 4H), 1.19 (m, 4H), 1.12 (d, syn CH_3, 3H), 0.91 (m, 1H), 0.81 (d, anti CH_3, 3H), 0.4–0.7 (m, 4H), 0.36 (bd, 1H). HRMS: calcd for C_9H_{14} 122.1095, found 122.1086.

In a 50-mL round-bottom flask was placed 0.15 g (0.61 mmol, 2.35 equiv) of the mixture of *syn*- and *anti*-methyl derivatives and 10 mL of diethyl ether. To this was added 150 mg (0.26 mmol) of Ziese's dimer, and the solution was stirred for 3 h at room temperature. At completion, the volume of solvent was reduced to 1 mL and the remainder was triturated three times with pentane and filtered to give a yellow solid residue, which was treated with 2 equiv of pyridine in 20 mL of diethyl ether. This solution was stirred for 15 min at room temperature, after which the solvent was reduced to 1 mL and subsequently triturated with pentane three times and filtered. A 0.25-g amount of a bright yellow solid residue, *syn*-**9**, was obtained (90% yield). ^{1}H NMR ($CDCl_3$; ppm): 3.56 (m, 1H), 2.99 (d, 1H), 2.87 (bd, 1H), 2.79 (dd, 1H), 2.54 (m, 1H), 2.16 (d, 1H), 1.1–1.8 (m, 5H), 0.56 (d, 3H). ^{13}C NMR (ppm ($^1J_{Pt-C}$, Hz)): 1.33 (351), 59.2 (97), 12.1 (401), 40.2, 28.8, 28.6, 37.8, 37.4, 17.1. Anal. Calcd for $C_{19}H_{24}PtCl_2N_2$: C, 41.77; H, 4.43; Cl, 12.98; N, 5.13. Found: C, 41.43; H, 4.65; Cl, 12.67; N, 4.91.

Preparation of Complexes 10 and 11. In a 50-mL round-bottom flask equipped with stirbar and condenser was placed compound **7b** or **8b** (150 mg, 0.27 mmol), methylene chloride (25 mL), and 0.4 g (1.07 mmol) of pyridinium dichromate. The mixture was stirred at room temperature for 24 h followed by rotavaporation and chromatography on a short Florisil column using CH_2Cl_2. The resulting light yellow solution was rotavaporated to give a yellow oil, which solidified upon trituration with pentane. Yields ranged from 75 to 85%. **10**: ^{13}C NMR ($CDCl_3$; ppm (J_{Pt-C}, Hz)) 4.35 (352), 55.6 (106), 15.2 (380), 40.5, 29.1, 37.8, 39.7, 29.1, 208.5 (22). **11**: ^{13}C NMR ($CDCl_3$; ppm (J_{Pt-C}, Hz)) 4.8 (348), 53.9 (103), 15.7 (377), 40.8, 29.2, 35.9, 41.4, 27.5, 208.4 (10). Anal. Calcd for **10** and **11** ($C_{19}H_{22}ON_2PtCl_2$): C, 40.78; H, 3.97; Cl, 12.51; N, 5.01. Found for **10**: C, 41.20; H, 3.62; Cl, 12.67; N, 4.73. Found for **11**: C, 41.23; H, 3.71; Cl, 12.81; N, 5.27.

Synthesis of *syn*-12. *syn*-**12** was synthesized by methylation of alcohols **3a** and **3b**. This methylation was achieved by treating the mixture, 2.5 g of **3a** and **3b**, with 2.2 equiv of sodium hydride and 1.0 equiv of methyl iodide in dry tetrahydrofuran. This solution was stirred at room temperature for 36 h, after which the reaction was quenched by addition of water followed by extraction with diethyl ether three times. The combined washings were rotavaporated, and the residue was vacuum-distilled at 55 °C (8 mmHg) to give a mixture (1.7 g) of *syn*- and *anti*-hydroxymethyl ethers as a colorless oil (63% yield, anti to syn ratio 2.2). Syn: ^{13}C NMR ($CDCl_3$; ppm) 16.6, 21.4, 30.6, 29.9, 36.0, 70.7, 58.1; HRMS calcd for $C_{10}H_{16}O$ 152.1201, found 152.1193. Anti: ^{13}C NMR ($CDCl_3$; ppm) 13.6, 20.9, 28.5, 29.5, 35.7, 75.7, 58.3; HRMS calcd for $C_{10}H_{16}O$ 152.1201, found 152.1196.

To 3.2 equiv (0.25 g, 1.63 mmol) of the epimeric mixture of syn and anti ethers in a 50-mL round-bottom flask was added 20 mL of diethyl ether. Subsequently 1 equiv (0.15 g, 0.26 mmol), equal to the amount of the syn isomer, of Zeise's dimer was added and the solution stirred for 20 min at room temperature to ensure complete reaction. All but 1 mL of the solvent was removed, followed by trituration of the precipitate using three 20-mL portions of pentane. The pentane washings were collected to yield pure anti ether. The remaining precipitate was dried under a stream of dry N_2, and 20 mL of diethyl ether containing 2 equiv of pyridine was added. The solution was stirred at room temperature for 15 min followed by trituration with pentane, yielding 0.23 g of the yellow solid **12** (80% yield). ^{13}C NMR ($CDCl_3$; ppm (J_{Pt-C}, Hz)): C1 0.5 (373), C2 57.5 (97), C3 13.7 (394), C4 38.3, C5 29.1, C6 28.8, C7 37.6, C8 40.5, C9 73.5 (15), C10 58.0. Anal. Calcd for $C_{20}H_{26}PtCl_2N_2$: C, 41.67; H, 4.55; Cl, 12.30; N, 4.86. Found: C, 41.80; H, 4.41; Cl, 12.03; N, 4.98.

Reaction of Complex 6 with Ethyl Diazoacetate to Give (*E*)- and (*Z*)-13. To a solution of 0.15 g (0.28 mmol) of complex **6** in 2 mL of chloroform was added 10 equiv (319 mg) of ethyl diazoacetate slowly over 20 min. The solution was then stirred at room temperature for an additional 30 min and concentrated. Chromatography of the resulting solution on silica gel using a 60% pentane–40% ether solution as the eluent afforded 51 mg of the products (*E*)- and (*Z*)-**13** (93% yield). (*E*)-**13**: ^{1}H NMR ($CDCl_3$; ppm) 2.65 (m, 1H), 2.56 (m, 1H), 6.87 (dd, 1H), 5.77 (d, 1H), 4.17 (q, 2H), 1.30 (t, 3H), 5.69 (m, 1H), 4.86 (d, 1H), 4.90 (d, 1H), 1.1–1.4 (m, 3H), 1.9–2.1 (m, 3H); ^{13}C NMR ($CDCl_3$; ppm) 44.2, 39.5, 42.6, 31.2, 31.6, 152.9, 119.5, 166.9, 60.1, 14.0, 142.5, 112.9; HRMS calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1306. (*Z*)-**13**: ^{1}H NMR ($CDCl_3$; ppm) 3.66 (m, 1H), 2.56 (m, 1H), 6.04 (dd, 1H), 5.63 (d, 1H), 4.17 (q, 2H), 1.30 (t, 3H), 5.69 (m 1H), 4.86 (d, 1H), 4.90 (d, 1H), 1.1–1.4 (m, 3H), 1.9–2.1 (m, 3H); ^{13}C NMR ($CDCl_3$; ppm) 44.4, 40.6, 38.9, 31.8, 32.1, 154.7, 118.1, 166.5, 59.8, 14.0, 142.7, 112.7; HRMS calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1320.

Reaction of 7b with Ethyl Diazoacetate. To a solution of 0.15 g (0.27 mmol) of **7b** in 2 mL of chloroform was added 10 equiv (308 mg) of ethyl diazoacetate slowly over 20 min. After the solution was stirred at room temperature for 30 min, it was chromatographed on silica gel using a 60% pentane–40% ether solution as the eluent and afforded 47 mg of the products (*E*)- and (*Z*)-**14** (79% yield). (*E*)-**14**: ^{1}H NMR ($CDCl_3$; ppm) 2.76 (m, 1H), 2.68 (m, 1H), 6.88 (dd, 1H), 5.74 (d, 1H), 4.22 (q, 2H), 1.28 (t, 3H), 4.9–5.1 (m, 2H), 4.20 (d, 2H), 1.0–1.5 (m, 3H), 1.8–2.1 (m, 3H); ^{13}C NMR ($CDCl_3$; ppm) 38.5, 40.3, 38.3, 32.4, 32.7, 152.5, 119.7, 166.8, 60.8, 14.0, 124.0, 139.4, 67.0. (*Z*)-**14**: ^{1}H NMR ($CDCl_3$; ppm) 3.81 (m, 1H), 2.68 (m, 1H), 6.06 (dd, 1H), 5.64 (d, 1H), 4.22 (q, 2H), 1.28 (t, 3H), 4.9–5.1 (m, 2H), 4.19 (d, 2H), 1.0–1.5 (m, 3H), 1.8–2.1 (m, 3H); ^{13}C NMR ($CDCl_3$; ppm) 42.8, 41.4, 39.1, 31.3, 32.2, 154.2, 118.4, 166.4, 60.8, 14.0, 123.6, 139.1, 66.9. These complexes have been previously reported.[3]

Reaction of 8b with Ethyl Diazoacetate. This reaction was conducted in a manner analogous to that used for **7b**. The yield of isomers was 75%. (*E*)-**15**: ^{1}H NMR ($CDCl_3$; ppm) H1 2.63 (m, 1H), H3 2.61 (m, 1H), H6 6.87 (dd, 1H), H7 5.72 (d, 1H), H9 4.18 (q, 2H), H10 1.25 (t, 3H), H11, H12 5.45–5.7 (m, 2H), H13 4.20 (d, 2H), H2, H4, H5 1.0–1.5 (m, 3H), 1.72 (m, 3H); ^{13}C NMR ($CDCl_3$; ppm) C1 42.9, C2 40.0, C3 35.7, C4 29.9, C5 32.4, C6 152.7, C7 119.6, C8 166.4, C9 63.2, C10 14.0, C11 123.9, C12 139.2 C13 68.2; HRMS calcd for $C_{13}H_{20}O_3$ 224.1412, found 224.1404. (*Z*)-**15**: ^{1}H NMR ($CDCl_3$; ppm) H1 3.74 (m, 1H), H3 2.61 (m, 1H), H6 6.05 (dd, 1H), H7 5.62 (d, 1H), H9 4.18 (q, 2H), H10 1.25 (t, 3H), H11, H12 5.45–5.7 (m, 2H), H13 4.25 (d, 2H), H2, H4, H5 1.0–1.5 (m, 3H), 1.7–2.1 (m, 3H); ^{13}C NMR ($CDCl_3$; ppm) C1 42.5, C2 41.0, C3 39.4, C4 29.8, C5 32.7, C6 154.5, C7 118.3, C8 166.3, C9 63.2, C10 14.0, C11 123.6, C12 139.6, C13 68.4; HRMS calcd for $C_{13}H_{20}O_3$ 224.1412, found 224.1404.

Reaction of *syn*-9 with Ethyl Diazoacetate. To a solution of 0.15 g (0.26 mmol) of *syn*-**9** and 2 mL of chloroform was added 10 equiv (297 mg) of ethyl diazoacetate slowly over 20 min with stirring at room temperature for an additional 30 min. Concentration and chromatography of the resulting solution on silica gel using a 60% pentane–40% ether solution as the eluent afforded 57 mg of the products (*E*)- and (*Z*)-**16** in 91% yield. (*E*)-**16**: ^{1}H NMR ($CDCl_3$; ppm) 2.65 (m, 1H), 2.83 (m, 1H), 6.88 (dd, 1H), 5.72 (d, 1H), 4.24 (q, 2H), 1.28 (t, 3H), 5.2–5.4 (m, 2H), 1.56 (d, 3H), 1.1–1.4 (m, 3H), 1.8–2.1 (m, 3H); ^{13}C NMR ($CDCl_3$; ppm) 42.7, 40.2, 37.8, 31.3, 32.2, 153.0, 119.4, 166.8, 60.5, 14.0, 135.1, 122.9, 14.8; HRMS calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1446. (*Z*)-**16**: ^{1}H NMR ($CDCl_3$; ppm) 3.79 (m, 1H), 2.83 (m, 1H), 6.10 (dd, 1H), 5.62 (d, 1H), 4.74 (q, 2H), 1.28 (t, 3H), 5.2–5.4 (m, 2H), 1.56 (d, 3H), 1.1–1.4 (m, 3H), 1.8–2.1 (m, 3H); ^{13}C NMR ($CDCl_3$; ppm) 39.1, 41.3, 37.9, 32.3, 32.6, 154.8, 118.1, 166.5, 60.5, 14.0, 135.3, 123.0, 15.0; HRMS calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1462.

Reaction of 10 with Ethyl Diazoacetate. To a stirred solution of **10** (100 mg, 0.18 mmol) in 2 mL of chloroform was added 1.3 equiv (26 mg, 0.23 mmol) of ethyl diazoacetate slowly over 30 min, this mixture was stirred for another 30 min. Chromatography of the resulting solution on silica gel using a 60% pentane–40% ether solution gave a 91% yield of (*E*)- and (*Z*)-**17** (*E*/*Z* = 1.6): ^{1}H NMR ($CDCl_3$; ppm) 1.0–2.3 (m, 2H), 2.76

(m, 2H), 4.0–4.4 (m, 4H), 4.7 (d, 1H), 4.9 (d, 1H), 5.87 (m, 2H), 6.1 (dd, 1H), 6.5 (m, 2H), 6.88 (dd, 1H), 10.02 (d, 2H); HRMS calcd for $C_{13}H_{18}O_3$ 222.1256, found ((*E*)-**17**) 222.1248, ((*Z*)-**17**) 222.1246.

Reaction of 11 with Ethyl Diazoacetate. This reaction was conducted in a manner identical with that for **10** above to give an 86% yield of isomers (*E*)- and (*Z*)-**18** in the ratio *E*/*Z* = 1.4: ^{1}H NMR ($CDCl_3$; ppm) 9.46 (d, 2H), 6.89 (dd, 1H), 6.74 (dd, 2H), 6.06 (dd, 1H), 5.77 (d, 1H), 5.69 (d, 1H), 5.8–5.5 (m, 2H), 4.5–4.0 (m, 4H), 2.76 (m, 2H), 2.3–1.5 (m, 2H), 1.5–1.0 (m, 2H); HRMS calcd for $C_{13}H_{18}O_3$ 222.1256, found ((*E*)-**18**) 222.1259, ((*Z*)-**18**) 222.1252.

Reaction of Complex 12 with Ethyl Diazoacetate. To a solution of 0.15 g (0.28 mmol) of complex **12** and 2 mL of chloroform was added 10 equiv (319 mg) of ethyl diazoacetate slowly over 20 min. The solution was stirred at room temperature for an additional 30 min. Chromatography of the resulting solution on silica gel using a 60% pentane–40% ether solution as the eluent afforded 54 mg of the products (*E*)- and (*Z*)-**19**: (88% yield); the *E*/*Z* ratio was 1.7. (*E*)-**19**: ^{1}H NMR ($CDCl_3$; ppm) 2.64 (m, 1H), 2.83 (m, 1H), 6.87 (dd, 1H), 5.73 (d, 1H), 4.15 (q, 2H), 1.25 (t, 3H), 5.35–5.5 (m, 2H), 4.00 (d, 1H), 3.26 (s, 3H), 1.1–1.4 (m, 3H), 1.7–2.1 (m, 3H); ^{13}C NMR ($CDCl_3$; ppm) 42.7, 41.4, 38.4, 31.3, 32.7, 154.3, 118.4, 166.7, 60.5, 14.1, 125.0, 137.8, 68.1, 57.7; HRMS calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1572. (*Z*)-**19**: ^{1}H NMR ($CDCl_3$; ppm) 3.79 (m, 1H), 6.05 (dd, 1H), 5.63 (d, 1H), 4.15 (q, 2H), 1.25 (t, 3H), 5.35–5.5 (m, 2H), 3.92 (d, 2H), 3.26 (s, 3H), 1.1–1.4 (m, 3H), 1.7–2.1 (m, 2H); ^{13}C NMR ($CDCl_3$; ppm) 39.1, 40.4, 38.5, 32.2, 32.5, 152.5, 119.6, 166.4, 60.5, 14.1, 125.1, 138.0, 68.2, 57.7; HRMS calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1572.

Reaction of Complex 6 with 2,2,2-Trifluorodiazoethane To Give (*E*)- and (*Z*)-20. To a solution of 150 mg (0.28 mmol) of complex **6** and 10 mL of chloroform was added 10 mL of a prepared cold ether solution of 2,2,2-trifluorodiazoethane. The solution of 2,2,2-trifluorodiazoethane was prepared by the method of Gilman and Jones.[14] The resulting mixture was stirred for 4 h at room temperature. Subsequently, the volume was reduced to near dryness and the residue was dissolved in a 1:1 mixture of pentane and diethyl ether and chromatographed on a short column of alumina. The fractions were combined, and the solvent was removed to give 0.05 g of a colorless oil, (*E*)- and (*Z*)-**20** (86% yield). (*E*)-**20**: ^{1}H NMR ($CDCl_3$; ppm) H1 2.63 (m, 1H), H1 2.59 (m, 1H), H6 6.35 (dd, 1H), H7 5.57 (m, 1H), H9 5.79 (m, 1H), H10 4.91 (d, 1H), 5.00 (d, 1H), H2, H4, H5 1.0–1.7 (m, 6H); ^{13}C NMR ($CDCl_3$; ppm (J_{C-F}, Hz)) C1 41.9, C2 39.4, C3 44.1, C4 31.7, C5 31.5, C6 144.2 (6.5), C7 116.7 (32.7), C8 123.2 (269), C9 113.0, C10 14.23; HRMS calcd for $C_{10}H_{13}F_3$ 190.0969, found 190.0968. (*Z*)-**20**: ^{1}H NMR ($CDCl_3$; ppm) H1 3.07 (m, 1H), H3 2.59 (m, 1H), H6 5.87 (dd, 1H), H7 5.50 (m, 1H), H9 5.79 (m, 1H), H10 4.91 (d, 1H), 5.00 (d, 1H), H2, H4, H5 1.0–1.7 (m, 6H); ^{13}C NMR ($CDCl_3$; (J_{C-F}, Hz)) C1 38.9, C2 40.7, C3 44.3, C4 31.7, C5 32.2, C6 147.4 (5.5), C7 116.9 (33.8), C8 123.0 (269), C9 113.0, C10 142.3; HRMS calcd for $C_{10}H_{13}F_3$ 190.0969, found 190.0948.

Reaction of Complex 7b with 2,2,2-Trifluorodiazoethane To Give (*E*)- and (*Z*)-21. To a solution of 150 mg (0.28 mmol) of complex **7b** and 10 mL of chloroform was added 10 mL of a prepared cold ether solution of 2,2,2-trifluorodiazoethane. The resulting mixture was stirred for 4 h at room temperature followed by volume reduction to near dryness. The residue (54 mg) was dissolved in $CDCl_3$ and analyzed by ^{1}H and ^{13}C NMR spectroscopy. (*E*)- and (*Z*)-**21** were formed in 91% yield by ^{1}H NMR. (*E*)-**21**: ^{1}H NMR ($CDCl_3$; ppm) H1 2.63 (m, 1H), H3 2.86 (m, 1H), H6 6.81 (dd, 1H), H11 4.21 (d, 2H), H2 1.8–2.1 (m, 2H), H4, H5 1.1–1.6 (m, 4H), H7, H9, H10 (m, 3H); ^{13}C NMR ($CDCl_3$; ppm (J_{C-F}, Hz)) C1 41.2, C2 42.5, C3 40.2, C4 34.0, C5 34.5, C6 146.1 (6), C7 118.7 (32.7), C8 123.4 (268), C9 126.7, C10 134.9, C11 63.0. (*Z*)-**21**: ^{1}H NMR ($CDCl_3$; ppm) H1 3.16 (m, 1H), H3 2.86 (m, 1H), H6 5.86 (dd, 1H), H11 4.21 (d, 2H), H2 1.8–2.1 (m, 2H), H4, H5 1.1–1.6 (m, 4H), H7, H(, H10 (m, 3H); ^{13}C NMR ($CDCl_3$; ppm (J_{C-F}, Hz)) C1 44.2, C2 43.8, C3 40.5, C4 32.7, C5 34.8, C6 149.1 (6), C7 119.1 (33.8), C8 123.1 (268), C9 125.3, C10 134.2, C11 63.0; HRMS calcd for $C_{11}H_{15}OF_3$ 220.1075, found ((*E*)-**21**) 220.1071, ((*Z*)-**21**) 220.1069.

Reaction of Complex 9 with 2,2,2-Trifluorodiazoethane To Give (*E*)- and (*Z*)-22. To a solution of 150 mg (0.28 mmol) of complex **9** and 10 mL of chloroform was added 10 mL of a prepared cold ether solution of 2,2,2-trifluorodiazoethane. The resulting mixture was stirred for 4 h at room temperature, and the volume was reduced to near dryness. The 0.06 g of residue was dissolved in $CDCl_3$ and analyzed by ^{1}H and ^{13}C NMR spectroscopy. (*E*)- and (*Z*)-**22** were formed in 84% yield via ^{1}H NMR (*E*/*Z* = 1.4). (*E*)-**22**: ^{13}C NMR ($CDCl_3$; ppm (J_{C-F}, Hz)) C1 42.1, C2 40.2, C3 37.7, C4 29.7, C5 32.3, C6 147.6 (5.5), C7 116.6 (32.7), C8 122.9 (270), C9 123.6, C10 135.0, C11 12.9. (*Z*)-**22**: ^{13}C NMR ($CDCl_3$; ppm (J_{C-F}, Hz)) C1 39.1, C2 41.4, C3 37.9, C4 31.3, C5 32.5, C6 144.5 (6.5), C7 116.8 (32.7), C8 122 (269), C9 123.6, C10 135.0, C11 12.9; HRMS calcd for $C_{11}H_{15}F_3$ 204.1126, found ((*E*)-**22**) 204.1125, ((*Z*)-**22**) 204.1129.

X-ray Crystallographic Data for 11. Crystal data: $C_{19}H_{22}N_2OCl_2Pt{\cdot}CHCl_3$, fw 679.8, triclinic, space group $P\bar{1}$, a = 9.710(2) Å, b = 10.886(3) Å, c = 11.515(2) Å, α = 80.98(2)°, β = 86.21(2)°, γ = 86.45(2)°, V = 1197.8(5) Å^3, Z = 2, D_{calc} = 1.88 g/cm^3, T = 25 °C, radiation Mo Kα (λ = 0.710 69 Å), μ = 64.9 cm^{-1}, R = 0.054, R_w = 0.052, S = 1.20, 263 parameters. Intensity data were taken as $\theta/2\theta$ scans on a Nicolet R3mE four-circle diffractometer for 8737 unique reflections in the range 4° < 2θ < 65°, of which 4425 with $I > 3\sigma(I)$ were used for structure solution and refinement. The data were corrected for Lorentz and polarization effects and for absorption by Gaussian integration (transmission factor range 0.164–0.878). No corrections for extinction were needed. The structure was solved from a Patterson synthesis for the platinum position. Non-hydrogen atoms were refined by block-cascade least squares with anisotropic thermal parameters, using statistical weighting.[15] Atomic scattering factors, including terms for anomalous dispersion, were taken from Cromer and Waber.[16] Calculated hydrogen positions were used with a common refined thermal parameter.

Acknowledgment. Support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and Johnson Matthey/Aesar/Alfa is gratefully acknowledged.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, and bond angles for complex **11** (2 pages). Ordering information is given on any current masthead page.

OM9302812

(14) Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1943**, *65*, 1458.

(15) Crystallographic calculations were done with the SHELXTL program package by G. M. Sheldrick: Siemens Analytical X-Ray Instruments, Inc. Madison, WI.

(16) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72–98, 149–150.