

by using standard heavy-atom methods and successive difference Fourier maps using the Enraf-Nonius software package "SDP-PLUS" (B.A. Frenz and Associates, College Station, TX 77840, 4th ed., 1981) on a PDP 11/44 computer. Scattering factors were taken from ref 15, and unit weights were used throughout. For 1 the final full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms gave final values of $R = 0.0544$ and $R_w = 0.0681$. The hydrogen atoms were either located or placed in their calculated positions with idealized geometries (C-H = 0.96 Å) with fixed isotropic thermal parameters. No chemically significant peaks were present in the final difference Fourier map which showed no features greater than $0.3 \text{ e}/\text{Å}^3$. Although data was collected out to $2\theta = 50.0^\circ$ for the crystal finally chosen for measurement, the rapid fall off in intensity meant that many high angle data were unobserved. This inevitably resulted in a lower than preferred data/parameter ratio. Nevertheless, we feel that the analysis was justified in that the molecular structure is more than adequately determined. For 2 hydrogen atoms were not located and the structure refined smoothly to give $R = 0.041$ and $R_w = 0.052$ (all atoms anisotropic).

Atomic thermal parameters and tables of observed and calculated structure factors and all bond lengths and angles for 1 and 2 are available.¹⁶

Acknowledgment. We thank the Dow Chemical Co., Midland, MI, the Robert A. Welch Foundation (F-816), the University Research Institute of the University of Texas at Austin, and the National Science Foundation (Grant CHE82-11883) for support. We also thank Johnson Matthey Inc. for a generous loan of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$. The X-ray diffractometer was purchased with funds from the National Science Foundation (Grant CHE82-05871) and the University of Texas at Austin.

Registry No. 1, 87555-81-5; 2, 87555-82-6; Cr, 7440-47-3; Ni, 7440-02-0; Rh, 7440-16-6.

Supplementary Material Available: Tables of atomic thermal parameters and structure factors for 1 and 2 and complete tables of atomic positional parameters and bond lengths and angles for 1 (69 pages). Ordering information is given on any current masthead page.

(15) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Volume 4.

(16) See paragraph at end of paper regarding supplementary material.

Synthesis and Rearrangement of (Bicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum(0) Complexes

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Platinum(0) complexes of a variety of halo-substituted bicyclo[2.2.1]hept-2-ene derivatives were prepared by displacement reactions between $\text{Pt}(\text{PPh}_3)_3$ and the requisite olefins. These complexes were characterized by elemental analysis, by ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy, and, in some cases, by the dissociation of the olefin ligand in solution. The rearrangement of selected haloolefin complexes to give (bicyclo[2.2.1]hept-2-en-2-yl)haloplatinum(II) derivatives was also investigated. The ease of rearrangement, which proceeded via the insertion of the platinum atom into the vinyl carbon-halogen bond, depended upon the identity of the halogen and the stability of the precursor (haloolefin)platinum(0) complex. In order to distinguish between the cis and trans isomers of (3-bromobicyclo[2.2.1]hept-2-en-2-yl)bromobis(triphenylphosphine)platinum, we carried out a structural determination on the trans isomer by single-crystal X-ray crystallography. Compound 31 crystallized in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 16.411$ (4) Å, $b = 19.340$ (8) Å, $c = 12.434$ (5) Å, and $\beta = 106.19$ (4)°. The calculated density was $1.703 \text{ g}/\text{cm}^3$ for four molecules in the unit cell. The unweighted R factor for the structure was 0.108, and data were collected by using a variable rate ω - 2θ scan technique and graphite-monochromatized $\text{Mo K}\alpha$ radiation. After Lorentz-polarization, absorption, and background corrections, 1640 reflections with $2\theta = 0$ - 60° were observed [$F_o^2 \geq 2\sigma(F_o^2)$].

Introduction

The interaction of strained organic molecules with transition-metal substrates has introduced new dimensions into the study of strain in organic chemistry. While some transition-metal systems promote the rearrangement of strained organic molecules,² other transition-metal systems form stable complexes with inherently unstable compounds.³

Bennett and Yoshida have recently reported the stabilization of the short-lived cyclic alkynes, cycloheptyne and cyclohexyne, as the bis(triphenylphosphine)platinum(0) complexes 1 and 2, respectively.⁴ Thus, reduction of the 1,2-dibromocycloalkenes 3 and 4 with sodium amalgam in the presence of tris(triphenylphosphine)-

(1) National Science Foundation Predoctoral Fellow, 1975-1978. Louise T. Dosdall Graduate Fellow, 1978-1979. Lubrizol Foundation Fellow, Summer, 1979.

(2) (a) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; pp 245-277. (b) Alper, H. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. 2, Chapter 3, pp 150-158.

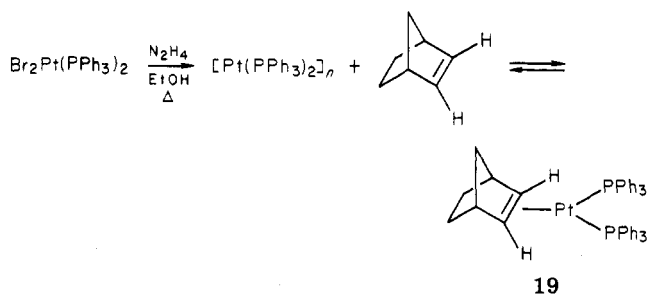
(3) For selected examples, see: (a) Fitzpatrick, J. D.; Watts, L.; Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* 1965, 87, 3254. (b) Roth, W. R.; Meier, J. D. *Tetrahedron Lett.* 1967, 2053. (c) Jason, M. E.; McGinney, J. A.; Wiberg, K. B. *J. Am. Chem. Soc.* 1974, 96, 6531. (d) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. *J. Ibid.* 1979, 101, 263. (e) Visser, J. P.; Ramakers, J. E. *J. Chem. Soc., Chem. Commun.* 1972, 178.

(4) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* 1971, 93, 3797. Bennett, M. A.; Yoshida, T. *Ibid.* 1978, 100, 1750.

olefin in tetrahydrofuran solution at 25 °C. Olefins which did not yield isolable complexes with **5** included bicyclo[2.2.1]hept-2-ene, 2-chloro-3-(trimethylsilyl)bicyclo[2.2.1]hept-2-ene, and 2-chloro-3-methylbicyclo[2.2.1]hept-2-ene.⁹ These results appear to be consistent with the need for a strong electronic bias in the platinum-olefin interaction. Whether the origin of this bias was primarily kinetic or thermodynamic could not be determined from this data alone. Electron-donating groups, such as methyl or trimethylsilyl, appear to offset the electron-withdrawing effect of a single halogen.

Several of the complexes in Table I dissociated or rearranged in solution. The dibromo complex **11** and the iodo bromo complex **12** did not dissociate in chloroform or tetrahydrofuran solution at 25 °C. The bromo chloro complex **15**, on the other hand, decomposed after several days in tetrahydrofuran solution (presumably owing to initial dissociation of the olefin ligand).^{10,11} This decomposition was more pronounced for the dichloro complex **16**, and the dissociation of the olefin could be followed by NMR spectroscopy in chloroform solution. This showed complete loss of the (dichlorobicyclo[2.2.1]hept-2-ene)-platinum complex after 24 h at 25 °C. The monobromo and monochloro complexes **17** and **18**, respectively, were even less stable in solution.

The parent complex of bicyclo[2.2.1]hept-2-ene, **19**, was desired in order to determine whether the ring strain itself imparted any stability to the platinum-olefin interaction. Complex **19** was prepared via the reaction of bicyclo[2.2.1]hept-2-ene with bis(triphenylphosphine)platinum, generated in situ by the reduction of dibromobis(triphenylphosphine)platinum(II) with hydrazine.¹² The extreme lability of the bicyclo[2.2.1]hept-2-ene complex **19** almost precluded its observation. In particular, the NMR spectrum of **19** in chloroform solution had to be taken immediately after preparation of the solution, since dissociation of olefin was evident after 10 min and seemed to be complete within 30 min. Thus, it could be concluded that electronic effects were of more significance than strain effects in determining the stability of these complexes.



NMR Spectra of (Bicyclo[2.2.1]hept-2-ene)platinum(0) Complexes. The ¹H NMR spectra of the (olefin)bis(triphenylphosphine)platinum complexes prepared in this study are presented in Table II. Several features of these NMR spectra merit discussion. In the 2,3-dihalo-substituted complexes **11**, **12**, **15**, and **16**, the bridgehead (allylic) proton resonances appeared between

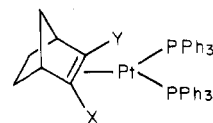
(9) For the preparation of these 2,3-disubstituted bicyclo[2.2.1]hept-2-ene derivatives, see ref 5a and 5c.

(10) The decomposition of the olefin complexes was apparent when the pale yellow solutions turned deep red; only red oily solids could then be obtained from these solutions. These solids resembled those reported in the decomposition of tris(triphenylphosphine)platinum in refluxing benzene.¹¹

(11) Taylor, N. J.; Chieh, P. C.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* 1975, 448. Gillard, R. D.; Ugo, R.; Cariati, F.; Cenini, S.; Bonati, F. *Ibid.* 1966, 869.

(12) Greaves, E. O.; Lock, C. J.; Maitlis, P. M. *Can. J. Chem.* 1968, 46, 3879.

Table II. ¹H NMR Spectra of (Bicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum Complexes

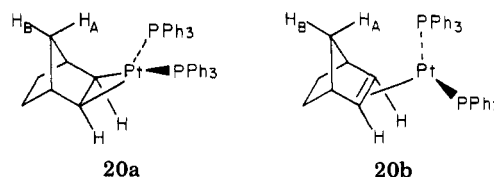


compd	NMR (CDCl ₃), δ
11 , X = Br, Y = Br	7.20 (30 H, s), 2.35 (2 H, t, ^a <i>J</i> = 16 Hz), 2.0-1.0 (5 H, m), 0.85 (1 H, d, <i>J</i> = 9 Hz)
12 , X = Br, Y = I	7.18 (30 H, br s), 2.45 (1 H, t, ^a <i>J</i> = 16 Hz), 2.28 (1 H, t, <i>J</i> = 16 Hz), 2.0-1.0 (5 H, m), 0.90 (1 H, d, <i>J</i> = 8 Hz)
15 , X = Br, Y = Cl	7.15 (30 H, br s), 2.35 (1 H, t, ^a <i>J</i> = 17 Hz), 2.20 (1 H, t, <i>J</i> = 17 Hz), 1.9-1.0 (5 H, m), 0.75 (1 H, d, <i>J</i> = 8 Hz)
16 , X = Cl, Y = Cl	7.15 (30 H, br s), 2.28 (2 H, t, ^a <i>J</i> = 19 Hz), 2.0-1.0 (5 H, m), 0.70 (1 H, d, <i>J</i> = 9 Hz)
17 , X = Br, Y = H	7.20 (30 H, m), 2.8 (1 H, br m), 2.45 (1 H, br m), 2.25 (1 H, br m), 1.75-1.0 (5 H, m), 0.50 (1 H, br s)
18 , X = Cl, Y = H	7.15 (30 H, br s), 2.35 (1 H, t, ^a <i>J</i> = 25 Hz), 2.10 (1 H, t, ^a <i>J</i> = 25 Hz), 1.75-0.9 (5 H, m), 0.40 (1 H, d, <i>J</i> = 8 Hz)
19 , X = H, Y = H	7.15 (30 H, br s), 2.30 (2 H, br, t, ^a <i>J</i> = 65 Hz), 2.20 (2 H, br m), 1.5-0.7 (5 H, m), 0.10 (1 H, d, <i>J</i> = 9 Hz)

^a The triplet consisted of the Pt-coupled doublet centered about an uncoupled singlet.

δ 2.45-2.20; these represent upfield shifts of 0.6-0.8 ppm, relative to the free olefins. Furthermore, the bridgehead protons in the complexes exhibited satellite peaks due to coupling with the platinum atom (¹⁹⁵Pt, *I* = 1/2, 33.8% natural abundance). The magnitude of the coupling constant *J*(H-C-C-Pt) varied from 16 to 25 Hz. The assignment of the allylic hydrogen signals in the 2-bromo- and 2-chlorobicyclo[2.2.1]hept-2-ene complexes **17** and **18**, respectively, was difficult, due to overlap with the olefinic hydrogen atom resonances. The olefinic hydrogen atoms in the parent bicyclo[2.2.1]hept-2-ene complex **19** appeared as a triplet [*J*(Pt-C-H) = 65 Hz] at δ 2.30; this is an upfield shift of 3.7 ppm relative to the free olefin. The net shielding of the olefinic protons that is observed in metal-olefin complexes has been described by Salomon and Kochi in terms of the relative contributions of σ and π bonding to the metal-olefin interaction.¹³

Each complex also showed a one-proton doublet (*J* = 8-9 Hz) between δ 0.85 and 0.10; this doublet was always the most shielded resonance and was well-separated from the rest of the hydrocarbon resonances, which occurred in a broad peak between δ 1.7 and 1.0. This upfield doublet has been assigned in each case to a proton on C-7 of the bicyclo[2.2.1]hept-2-ene complex.¹⁴ This proton would be oriented directly toward the platinum atom, if a structure such as **20a** or **20b** is assumed for the platinum-(0)-olefin complexes. Such a structure would result from



(13) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* 1973, 95, 1889.

(14) A similar effect has been observed for a (norbornadiene)manganese complex: Fritz, H. P.; Keller, H. *J. Chem. Ber.* 1963, 96, 1676.

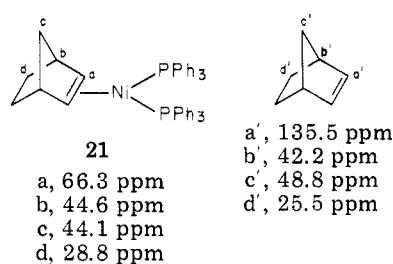
Table III. ^{13}C NMR Spectra of (Bicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum Complexes^{a-c}

compd	chem shift of carbons			compd	chem shift of carbons		
	1,4	7	6,5		1,4	7	6,5
11, X = Br, Y = Br	50.69	40.65	26.70	6, X = Br, Y = Br	51.42	46.80	25.53
12, X = Br, Y = I	52.44, 50.22	42.03	29.42, 26.88	8, X = Br, Y = I	55.00, 51.70	47.20	25.20
15, X = Br, Y = Cl	50.94, 49.67	39.82	26.84, 25.60	X = Br, Y = Cl	51.19, 49.94	46.45	25.88, 25.57
16, X = Cl, Y = Cl	50.00 ^d	38.90 ^d	25.40 ^d	X = Cl, Y = Cl	49.24	45.88	25.69

^a Spectra were run in deuteriochloroform at 20 MHz and were proton decoupled. ^b Only the aliphatic carbon signals are reported here. ^c Chemical shifts are reported in parts per million downfield of tetramethylsilane. ^d Partial dissociation of the olefin was observed during the course of data acquisition; the spectrum appeared as a sum of peaks due to free and coordinated olefin.

coordination of the platinum from the least hindered side of the olefin. Structurally, platinum(0)-olefin complexes are characterized by an almost square-planar arrangement of principally bonded atoms around platinum, such that the plane of the double bond (π and π^* orbitals) lies close to the plane of the platinum-olefin bond.⁸ The hydrogen atom (H_A) that is syn to the platinum would be expected to show a considerable upfield shift¹⁴ and would be geminally coupled to H_B ($J_{AB} = 8\text{--}12$ Hz).¹⁵

In this study, ^{13}C NMR and ^{31}P NMR spectra were recorded for these platinum-bicyclo[2.2.1]hept-2-ene complexes with reasonable stability in solution (vide infra), i.e., the 2,3-dihalo-substituted derivatives 11, 12, 15, and 16. The ^{13}C NMR spectra reinforced the trend observed in the ^1H NMR spectra, namely, the methano bridge carbon atom (C-7) showed a significant perturbation (upfield shift) upon coordination to the metal atom (Table III). The magnitude of the shift varied from 5.2 to 6.9 ppm. The bridgehead (allylic) carbon atoms experienced a much diminished effect; i.e., the upfield shift was in the range 0.3–2.5 ppm. (The dichloride complex 16 actually showed a downfield shift of 0.75 ppm for the bridgehead carbon.) Neither the quaternary (vinylic) carbon resonances nor the satellites due to splitting of the carbon atom resonances by platinum were detected. For comparison purposes, literature data for (bicyclo[2.2.1]hept-2-ene)-bis(triphenylphosphine)nickel (21),^{16c} relative to the free olefin,¹⁷ are presented.



The ^{31}P NMR spectra of the (dihalobicyclo[2.2.1]hept-2-ene)platinum complexes are reported in Table IV. Calibrated chemical shift measurements (relative to an external standard) were made for only two complexes, 11

Table IV. ^{31}P NMR Spectra of (Bicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum Complexes^a

compd	chem shift ^b	$^1J(^{195}\text{Pt}-^{31}\text{P})$
11, X = Br, Y = Br	-26.64	3292
12, X = Br, Y = I	$\nu_A = -24.97$, ^c $\nu_B = -24.01$ ($J_{AB} = 31.7$ Hz)	3321
15, X = Br, Y = Cl	not calibrated ^c ($\Delta\nu_{AB} = 34.83$ Hz, $J_{AB} = 32.3$ Hz)	3283
16, X = Cl, Y = Cl	not calibrated	3277

^a Spectra were run at 40.5 MHz and were ^1H decoupled. ^b Chemical shifts are reported in ppm downfield of 85% phosphoric acid as external standard. ^c These spectra showed AB quartets; parameters were calculated on this basis.

and 12. For the dibromide complex, the deshielding of coordinated triphenylphosphine produced a chemical shift difference of -32.64 ppm, relative to free ligand.¹⁸ The downfield shift is consistent with that observed in most transition-metal-phosphine complexes; it has not been possible to analyze these chemical shift differences in terms of the bonding of the metal and phosphorus atoms.¹⁹ More information has generally been deduced from the magnitude of the metal-phosphorus spin-spin coupling constants. The values of $^1J(^{195}\text{Pt}-^{31}\text{P})$ varied between 3277 and 3321 Hz for the four complexes studied. These values compare well with those observed for the ethylene complex 22¹⁸ or the hexafluoro-2-butyne complex 23²⁰ but are larger than those observed for the tetrafluoroethylene complex 24.²⁰ An increase in $J(\text{Pt}-\text{P})$ can be correlated with an increase in the s character of the platinum-phosphorus bond, due either to decreases in the C-Pt-C interbond angles²⁰ or to a decreasing trans influence of the trans ligand.^{19a}

Part 2. Isomerization Reactions and Related Stability Studies. Stability of (Bicyclo[2.2.1]hept-2-ene)platinum(0) Complexes. This study involved a detailed investigation of the effect which substituents on

(15) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 272.

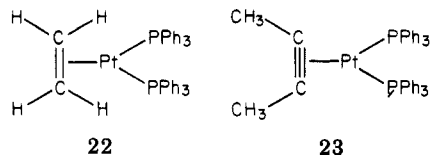
(16) (a) Gallazzi, M. C.; Hanlon, T. L.; Vitulli, G.; Porri, L. *J. Organomet. Chem.* 1971, 33, C45. (b) Gallazzi, M. C.; Porri, L.; Vitulli, G. *Ibid.* 1975, 97, 131. (c) Hoffmann, E. G.; Jolly, P. W.; Küsters, A.; Mynott, R.; Wilke, G. Z. *Naturforsch., B: Anorg. Chem., Org. Met.* 1976, 31B, 1712. (d) Tolman, C. A. *J. Am. Chem. Soc.* 1974, 96, 2780.

(17) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972; p 61.

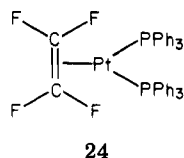
(18) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* 1972, 94, 2669.

(19) (a) Pregosin, P. S.; Venanzi, L. M. *Chem. Br.* 1978, 14, 276. (b) Nixon, J. F.; Pidcock, A. *Annu. Rev. NMR Spectrosc.* 1969, 2, 345.

(20) Kennedy, J. D.; McFarlane, W.; Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* 1976, 874.



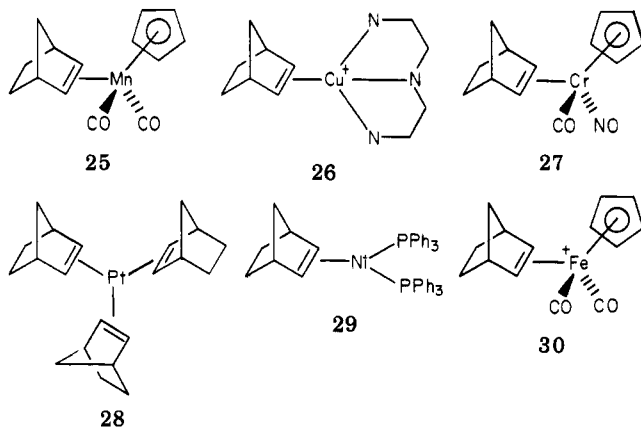
chem shift -32 ppm^{18}
 $J(\text{Pt-P})$ 3660 Hz



chem shift -25.7 ppm^{20}
 $J(\text{Pt-P})$ 2545 Hz

the double bond have on the stability of (bicyclo[2.2.1]hept-2-ene)metal complexes; although a large number of transition-metal complexes of the parent olefin have been described, detailed evaluations of substituent effects do not seem to have been made. Bicyclo[2.2.1]hept-2-ene complexes with copper,^{13,21} silver,²² gold,²³ manganese,²⁴ rhodium,²⁵ palladium,²⁶ nickel,¹⁶ platinum,²⁷ chromium,²⁸ and iron²⁹ have been prepared. The exo orientation of the metal with respect to the bicyclo[2.2.1]hept-2-ene unit has been verified for the manganese, copper, chromium, platinum, nickel, and iron complexes 25–30, respectively, shown below. Furthermore, these complexes showed the same type of ¹H NMR spectra as those reported in this study, i.e., the olefinic hydrogen atoms were strongly shielded relative to the free olefin and the syn and anti protons on C-7 were sharply differentiated from one another due to the proximity of the syn proton to the metal atom. In the copper complex 26, the interaction of this syn C-7 proton with the copper atom manifested itself in an unusually short (nonbonded) hydrogen–copper distance of 2.01 Å.^{21a} It was felt that this copper–hydrogen interaction could have significant impact on the study of metal-induced C–H activation of coordinated olefins.

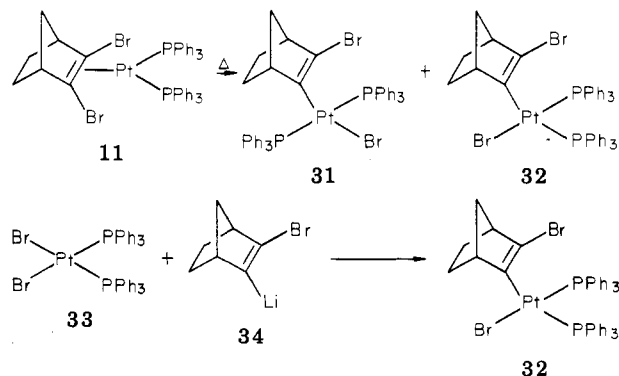
A direct comparison of the stability of the platinum–bicyclo[2.2.1]hept-2-ene complex 19 prepared in this study, relative to the other metal–bicyclo[2.2.1]hept-2-ene complexes 25–30 reported in the literature, was difficult, since reports on 25–30 did not contain data concerning the conditions required for olefin dissociation. The manganese complex 25 was reported to undergo a slow substitution reaction with triphenylphosphine, and the mechanism of this reaction was reported to involve initial dissociation



of the olefin.⁶ The nickel complex 29 would be expected to be more stable than the platinum analogue 19, if the trend observed in the related ethylene complexes applied.¹⁸ In this regard, it is interesting to note that (ethylene)-bis(triphenylphosphine)platinum was reported to be completely stable with respect to loss of ethylene in solution.¹⁸ The contrasting lability of the bicyclo[2.2.1]hept-2-ene complex 19 showed that the destabilizing electron-donating influence on the double bond of the “dialkyl” substitution by the skeleton of 19 effectively dominated the stabilizing influence provided by the ring strain.

Rearrangement of (Bicyclo[2.2.1]hept-2-ene)bis-(triphenylphosphine)platinum(0) Complexes. The (2,3-dibromobicyclo[2.2.1]hept-2-ene)platinum complex, 11, rearranged upon refluxing for 1 h in ethanol to give the (*trans*-3-bromobicyclo[2.2.1]hept-2-en-2-yl)platinum bromide complex, 31. A mixture of the *trans* and *cis* isomers, 31 and 32, was obtained when the complex 11 was recrystallized from hot tetrahydrofuran–ethanol. These isomers could be separated by fractional crystallization. A solution of the *cis* isomer in chloroform was gradually converted to the *trans* isomer over a 24-h period. This, and the exclusive formation of the *trans* isomer at higher temperatures, indicate that the *trans* isomer 31 is thermodynamically more stable than the *cis* isomer 32.

The structural identification of the rearranged derivatives 31 and 32 was based on elemental analysis, complete spectroscopic characterization, and an independent synthesis of the *cis* isomer by the transmetalation reaction of *cis*-dibromobis(triphenylphosphine)platinum (33) with 2-bromo-3-lithiobicyclo[2.2.1]hept-2-ene (34).³⁰ In general, the reactions of platinum dihalides with alkylolithium or Grignard reagents to give monoalkyl platinum compounds have been shown to proceed with retention of configuration about the square-planar platinum atom.³¹



(30) 2-Bromo-3-lithiobicyclo[2.2.1]hept-2-ene (34) has been described.^{5a} It is prepared via lithium–halogen exchange between *n*-butyllithium and 2,3-dibromobicyclo[2.2.1]hept-2-ene (6).

(21) (a) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* 1978, 100, 4918. (b) Salomon, R. G.; Kochi, J. K. *J. Organomet. Chem.* 1974, 64, 135.

(22) Lewandos, G. S.; Gregston, D. K.; Nelson, F. R. *J. Organomet. Chem.* 1976, 118, 363.

(23) Hüttel, R.; Reinheimer, H.; Nowak, K. *Tetrahedron Lett.* 1967, 1019; *Chem. Ber.* 1968, 101, 3761.

(24) (a) Angelici, R. J.; Loewen, W. *Inorg. Chem.* 1967, 6, 682. (b) Müller, J.; Herberhold, M. *J. Organomet. Chem.* 1968, 13, 399. (c) Herberhold, M.; Jablonski, C. R. *Chem. Ber.* 1969, 102, 767, 778.

(25) Winkhaus, G.; Singer, H. *Chem. Ber.* 1966, 99, 3602.

(26) (a) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1977, 271. (b) *J. Chem. Soc., Chem. Commun.* 1975, 449. (c) Atkins, R. M.; Mackenzie, R.; Timms, P. L.; Turney, T. W. *Ibid.* 1975, 764.

(27) (a) Green, M.; Laguna, A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1977, 10, 1010. (b) Ashley-Smith, J.; Douek, Z.; Johnson, B. F. G.; Lewis, J. *Ibid.* 1974, 2, 128.

(28) (a) Herberhold, M.; Alt, H.; Kreiter, C. G. *Justus Liebig's Ann. Chem.* 1976, 300. (b) Herberhold, M.; Alt, H. *J. Organomet. Chem.* 1972, 42, 407.

(29) (a) Nicholas, K. M. *J. Am. Chem. Soc.* 1975, 97, 3254. (b) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancredi, J.; Wells, D. *Ibid.* 1976, 98, 3495.

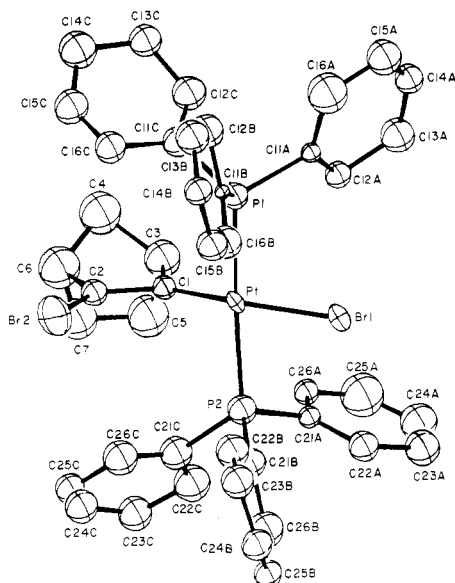
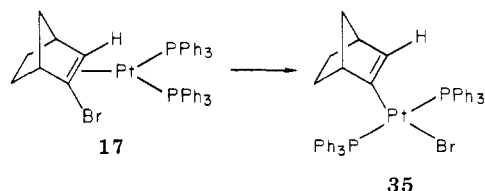


Figure 1. ORTEP drawing of **31**. Hydrogens have been omitted for clarity.

The unequivocal structure proof for the two isomers **31** and **32** was provided by a single-crystal X-ray diffraction study of the trans compound **31**.³² Although the precision of the bond length and bond angle measurements was limited by the very poor quality of the crystal (the crystals displayed some curvature and were very small), the assignment of stereochemistry was confirmed. An ORTEP drawing of the trans isomer is given in Figure 1. The atomic coordinates are listed in Table V.

The (2-bromo-3-iodobicyclo[2.2.1]hept-2-ene)platinum complex, **12**, was even more prone to rearrangement than the dibromide, and the cis and trans isomers **13** and **14** were obtained upon prolonged standing in chloroform or tetrahydrofuran solution. Furthermore, these isomers were not separated as easily as the dibromides, due to their facile interconversion. The ease of rearrangement of **12** to **13** and **14** explains why all three isomers were isolated from the reaction mixture after attempted reduction of 2-bromo-3-iodobicyclo[2.2.1]hept-2-ene with sodium amalgam and tris(triphenylphosphine)platinum (vide post), since the reaction mixture was worked up by slow crystallization in a drybox. (Allowing the olefin complex to stand in solution resulted in rearrangement.)

The (2-bromobicyclo[2.2.1]hept-2-ene)platinum complex, **17**, proved to be the most labile with respect to this intramolecular rearrangement sequence. Solutions of **17**



(31) (a) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 4020. (b) *Ibid.* **1959**, 705. (c) Rosevear, D. T.; Stone, F. G. A. *Ibid.* **1965**, 5275.

(32) The yellow crystals of $C_{14}H_{18}PtBr_2P_2$ belonged to the centrosymmetric monoclinic space group $P2_1/n$. The measured cell constants, $a = 16.411$ (4) Å, $b = 19.340$ (8) Å, $c = 12.434$ (5) Å, and $\beta = 106.19$ (4)°, gave a calculated density of 1.703 g/cm³ for four molecules in the unit cell. The unweighted R factor for the structure was 0.108. Data were collected on a fully automated Enraf-Nonius CAD4 diffractometer using a variable rate ω - 2θ scan technique and graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.710$ 69 Å). After Lorentz-polarization, absorption and background corrections, 1640 of the 4633 reflections with $2\theta = 0$ –60° were observed [$F_o^2 \geq 2\sigma(F_o^2)$].

in chloroform started to rearrange within minutes, and rearrangement to **35** was complete within 2 h. On a preparative scale, **35** was obtained in analytically pure form upon refluxing **17** in ethanol. The cis isomer was not detected. The trans stereochemistry was assigned on the basis of the thermal stability of **35** and because of the close relationship of its ¹H NMR spectrum to that of **31**.

The formation of the (bicyclo[2.2.1]hept-2-en-2-yl)platinum(II) compounds from the olefin complexes **11**, **12**, and **17** is an example of the insertion of platinum into a vinyl carbon-halogen bond. Similar rearrangements have been reported for tetrachloroethylene and (chlorotri-fluoroethylene)bis(triphenylphosphine)platinum complexes.³³ The mechanism of this rearrangement has been described as being intramolecular and proceeding without initial dissociation of the olefin ligand.³⁴

NMR Spectra of (Bicyclo[2.2.1]hept-2-en-2-yl)platinum(II) Compounds. The ¹H NMR spectra of the (bicyclo[2.2.1]hept-2-en-2-yl)platinum(II) complexes are reported in the Experimental Section. The most salient features of these spectra are the large differences in chemical shifts and coupling constants between the cis and trans isomers. The best characterized examples were found in the dibromo series **31** and **32**. The cis compound **32** showed a broad singlet at δ 7.15 for the aromatic protons, a 2 H triplet [$J(\text{Pt}-\text{C}-\text{C}-\text{H}) = 22$ Hz] at δ 2.33 for the bridgehead protons, a multiplet at δ 1.5–1.3 (4 H) for the protons on C-4 and C-5, and two 1 H doublets at δ 0.38 and 0.55 ($J = 8$ Hz) for the anti and syn C-7 protons, respectively. In contrast, the trans isomer **31** showed two broad singlets at δ 7.75 and 7.35 (2:3 ratio) for the aromatic protons, two signals for the different bridgehead protons at δ 2.45 (t, $J = 30$ Hz) and δ 2.08 (br s), a 2 H doublet at δ 0.83 ($J = 8$ Hz), an unsymmetrical triplet ($J = 8$ Hz, 3 H) at δ 0.10, and a 1 H doublet at δ 0.60 ($J = 8$ Hz) for the syn C-7 proton. The shielding of the syn C-7 proton was thus greater in the σ -bonded platinum(II) derivatives than in the platinum(0)- π -olefin complexes.

The ¹³C NMR and ³¹P NMR spectral data for the platinum(II) compounds **31** and **35** are reported in Table VI. The ¹³C NMR data for **31** do not show an upfield shift for C-7 (relative to olefin), whereas **35** does. The coupling constants (Pt-P) for **31** and **35** are rather large for phosphorus trans to phosphorus in a platinum(II) complex.¹⁹

Attempted Reductions of Platinum Complexes. Several attempts were made to convert either the dibromoolefin complex **11**, or its rearranged derivative **31**, into a bicyclo[2.2.1]hept-2-yne complex of platinum. Formally, this conversion would require the removal of two bromine atoms under reducing conditions. The olefin complex **11** was resistant to dehalogenation by sodium amalgam even at 65 °C, conditions under which the precursor dibromoolefin **6** was completely reduced. Similarly, neither sodium naphthalide nor *n*-butyllithium reacted with the dibromoolefin complex **11**. The trans rearranged derivative **31** was impervious to reduction by sodium amalgam or lithium metal at 25 °C. Hydrazine in ethanol at 60 °C did consume the platinum(II) compound **31**, but neither a bicyclo[2.2.1]hept-2-yne complex nor a compound resulting from addition of ethanol to such a complex could be detected in the reaction mixture. Sequential treatment of **31** with silver fluoroborate in acetone and triphenylphosphine in methylene chloride produced an isolable

(33) Bland, W. J.; Kemmitt, R. D. W. *Nature (London)* **1966**, *211*, 963; *J. Chem. Soc. A* **1968**, 1278.

(34) Bland, W. J.; Burgess, J.; Kemmitt, R. D. W. *J. Organomet. Chem.* **1968**, *14*, 201. See also: Rajaram, J.; Pearson, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 2103. Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712.

Table V. Atomic Coordinates and Thermal Parameters of All of the Non-Hydrogen Atoms of 31^a

atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
t	0.2462 (1)	0.1837 (1)	0.0769 (2)	0.00629 (8)	0.00109 (4)	0.0073 (1)	0.0014 (2)	0.0069 (2)	0.0018 (3)
r1	0.1196 (3)	0.2601 (3)	0.0669 (5)	0.0074 (3)	0.0019 (2)	0.0118 (6)	0.0025 (4)	0.0100 (6)	0.0031 (5)
r2	0.2999 (5)	0.0016 (3)	-0.0091 (7)	0.0167 (5)	0.0031 (2)	0.0202 (9)	-0.0041 (6)	0.0174 (10)	-0.0056 (8)
atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
P1	0.2471 (8)	0.2276 (7)	-0.097 (1)	4.2 (3)	C13C	0.453 (3)	0.239 (3)	-0.223 (5)	6.1 (15)
P2	0.2315 (9)	0.1432 (8)	0.246 (1)	5.0 (4)	C14C	0.457 (4)	0.166 (3)	-0.265 (5)	8.3 (18)
C1	0.351 (2)	0.136 (2)	0.097 (4)	3.2 (11)	C15C	0.400 (3)	0.125 (3)	-0.236 (5)	6.9 (16)
C2	0.379 (3)	0.067 (2)	0.071 (4)	4.0 (12)	C16C	0.327 (3)	0.135 (3)	-0.208 (4)	5.7 (14)
C3	0.439 (3)	0.163 (3)	0.139 (5)	7.7 (17)	C21A	0.256 (2)	0.215 (2)	0.345 (4)	2.8 (10)
C4	0.512 (4)	0.133 (4)	0.082 (6)	10.3 (21)	C22A	0.193 (3)	0.247 (3)	0.377 (4)	5.2 (13)
C5	0.478 (4)	0.132 (4)	0.260 (6)	10.2 (21)	C23A	0.215 (3)	0.310 (3)	0.455 (5)	7.1 (15)
C6	0.470 (4)	0.059 (4)	0.092 (6)	10.2 (21)	C24A	0.297 (3)	0.333 (3)	0.494 (5)	8.0 (17)
C7	0.492 (4)	0.061 (3)	0.215 (6)	9.6 (20)	C25A	0.352 (4)	0.297 (4)	0.455 (6)	11.0 (22)
C11A	0.251 (2)	0.325 (2)	-0.096 (3)	2.3 (8)	C26A	0.335 (3)	0.237 (2)	0.382 (4)	3.7 (11)
C12A	0.294 (3)	0.352 (2)	0.011 (4)	4.0 (12)	C21B	0.117 (3)	0.108 (2)	0.224 (4)	5.2 (13)
C13A	0.306 (3)	0.432 (3)	0.011 (5)	6.8 (16)	C22B	0.069 (3)	0.085 (3)	0.139 (5)	6.4 (15)
C14A	0.277 (3)	0.462 (3)	-0.103 (4)	4.9 (13)	C23B	-0.010 (3)	0.062 (3)	0.112 (4)	6.3 (15)
C15A	0.239 (3)	0.438 (3)	-0.200 (5)	7.2 (16)	C24B	-0.029 (3)	0.052 (3)	0.214 (4)	5.5 (14)
C16A	0.227 (4)	0.362 (4)	-0.204 (5)	9.5 (20)	C25B	0.018 (3)	0.061 (2)	0.320 (4)	4.5 (12)
C11B	0.160 (2)	0.199 (2)	-0.204 (3)	1.4 (9)	C26B	0.105 (3)	0.093 (3)	0.335 (5)	7.4 (17)
C12B	0.158 (3)	0.209 (3)	-0.321 (5)	6.4 (15)	C21C	0.304 (3)	0.071 (3)	0.333 (5)	6.4 (15)
C13B	0.082 (3)	0.177 (3)	-0.403 (4)	6.5 (14)	C22C	0.338 (4)	0.081 (3)	0.433 (5)	7.7 (17)
C14B	0.013 (3)	0.146 (2)	-0.379 (4)	4.5 (12)	C23C	0.394 (3)	0.021 (3)	0.489 (5)	6.6 (15)
C15B	0.018 (3)	0.139 (3)	-0.271 (4)	5.4 (14)	C24C	0.378 (3)	-0.035 (3)	0.412 (5)	6.3 (15)
C16B	0.090 (3)	0.168 (3)	-0.190 (5)	6.3 (15)	C25C	0.325 (3)	-0.050 (3)	0.317 (4)	5.1 (13)
C11C	0.331 (3)	0.207 (2)	-0.152 (4)	5.1 (14)	C26C	0.285 (3)	0.008 (3)	0.271 (5)	7.0 (16)
C12C	0.388 (3)	0.250 (3)	-0.164 (5)	6.7 (16)					

^a The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

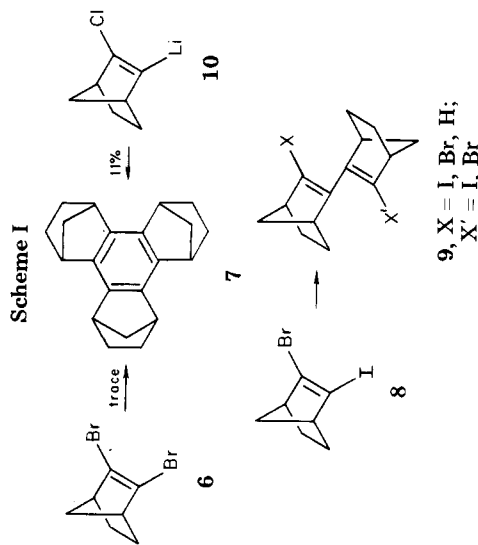
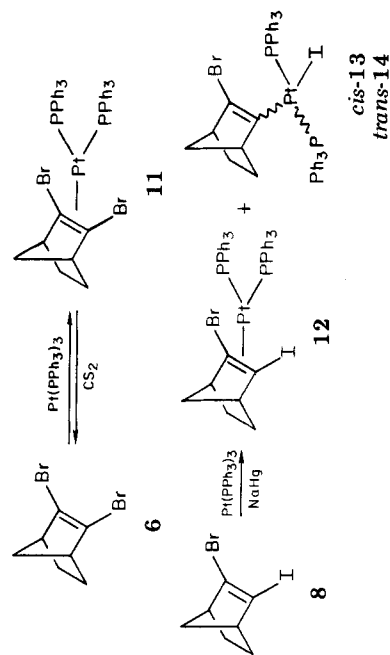
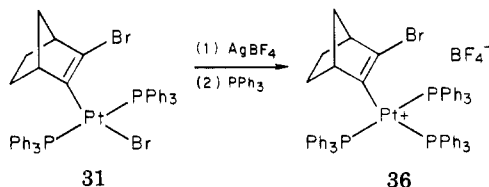
**Scheme II**

Table VI. ^{13}C NMR and ^{31}P NMR Spectra of (Bicyclo[2.2.1]hept-2-en-2-yl)platinum(II) Complexes

	31	35
^{13}C NMR ^a	135.07, 126.60, 130.04 (aromatic) ^b 54.36, 50.94 (C ₁ , C ₄) 48.54 (C ₇) 26.20, 25.92 (C ₅ , C ₆)	134.59, 126.90, 129.40 (aromatic) 53.15, 47.84 (C ₁ , C ₄) 42.21 (C ₇) 25.34 (C ₅ , C ₆)
^{31}P NMR ^c	-20.7 ($J_{\text{Pt-P}} =$ 3038 Hz)	-22.0 ($J_{\text{Pt-P}} =$ 3178 Hz)

^a Spectra were run at 20 MHz (CDCl_3) and were proton decoupled; all chemical shifts are reported in ppm downfield from Me_4Si . Signals due to C₂ and C₃ were not observed, presumably due to extensive coupling with both platinum and phosphorus. ^b The signal due to the quaternary aromatic carbon, which is attached to phosphorus, was not observed. ^c Spectra were run at 40.5 MHz (CDCl_3) and were proton decoupled; chemical shifts are reported in ppm downfield from 85% phosphoric acid (external standard).

cationic complex, which was assigned structure 36. It was hoped that the positive charge on platinum would facilitate the attack of active metals at the β -bromine atom. However, 36 proved to be inert toward reduction by sodium amalgam or lithium at 25 °C.



Treatment of tris(triphenylphosphine)platinum with 1.4 equiv of 2-bromo-3-iodobicyclo[2.2.1]hept-2-ene and 2.8 equiv of sodium amalgam at 25 °C produced a complex reaction mixture from which no reductively dehalogenated platinum(II) derivatives could be isolated after fractional crystallization. Instead, an 86% yield of a mixture of 12, 13, and 14 was obtained.

Summary

Dihalobicyclo[2.2.1]hept-2-enes reacted with tris(triphenylphosphine)platinum (5) to give platinum(0)-olefin complexes. The ease of formation of the olefin complexes from 5 can be ascribed to two factors: the high nucleophilicity of 5 due to the high σ donor capacity of the triphenylphosphine ligands and the ready dissociation of 5 to the "unsaturated", reactive bis(triphenylphosphine)platinum unit.³⁵ The extreme resistance of these halogen-bearing olefin-platinum complexes to reductive removal of the halogens makes such complexes potential protecting groups for certain halogenated olefins which must be exposed to reductive conditions.

Experimental Section

Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Melting points are uncorrected. Proton magnetic resonance spectra were recorded on Varian HFT-80 and Hitachi Perkin-Elmer R-24B nuclear magnetic resonance spectrometers. Carbon magnetic resonance

spectra were recorded on a Varian CFT-20 nuclear magnetic resonance spectrometer. Phosphorus magnetic resonance spectra were obtained on a Varian XL-100 nuclear magnetic resonance spectrometer. Infrared spectra were recorded on a Beckman Model 4240 infrared spectrophotometer as KBr pellets.

Platinum(0)-Olefin Complexes. Three procedures are described for the preparation of the platinum-olefin complexes. Method A, the most general procedure, was applied in the majority of cases.

(2,3-Dibromobicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum (11). Method A. A solution of 2,3-dibromobicyclo[2.2.1]hept-2-ene (6)^{3c} (1.13 g, 4.5 mmol) in 100 mL of freshly distilled tetrahydrofuran was added to tris(triphenylphosphine)platinum (4.0 g, 4.1 mmol) under argon at 25 °C. The solution was stirred for 18 h at ambient temperature and then concentrated in vacuo to yield a yellow gum. This gum was triturated with 70 mL of absolute ethanol to give 3.05 g (3.14 mmol, 78%) of 11 as a white solid: mp 172–177 °C dec; IR (KBr) 3070, 3050, 2965, 2940, 2910, 2865, 1960 (br), 1900 (br), 1820 (br), 1590, 1573, 1480, 1435, 1310, 1292, 1215, 1185, 1096, 1040, 1000, 775, 740, 690, 628, 530, 515, 505, 450, 420 cm^{-1} . An analytical sample was prepared via recrystallization from tetrahydrofuran-hexane: mp 175–180 °C dec. Anal. Calcd for $\text{C}_{43}\text{H}_{38}\text{PtBr}_2\text{P}_2$: C, 53.15; H, 3.94; Br, 16.45. Found: C, 53.16; H, 4.22; Br, 16.38.

(2,3-Dibromobicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum (11). Method B. To a solution of 6 (210 mg, 0.83 mmol) in 30 mL of dry toluene under argon was added (ethylene)bis(triphenylphosphine)platinum (500 mg, 0.67 mmol) at 25 °C. The mixture was stirred for 12 h at room temperature and filtered, and the filtrate was concentrated in vacuo. The resulting brown oil was triturated with hexane to give a beige solid. The product was recrystallized from tetrahydrofuran-hexane to give 260 mg (0.27 mmol, 40%) of 11 as yellow crystals: mp 175–180 °C dec; IR and NMR spectra were identical with those obtained from the previous preparation.

(2-Bromo-3-iodobicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum (12). Compound 12 was prepared according to method A. A solution of 2-bromo-3-iodobicyclo[2.2.1]hept-2-ene (8) (310 mg, 1.03 mmol) in 15 mL of freshly distilled tetrahydrofuran was added to tris(triphenylphosphine)platinum (1.0 g, 1.03 mmol) under argon at 25 °C. The solution was stirred for 18 h at 25 °C and then concentrated in vacuo. The residue was triturated with 40 mL of absolute ethanol to give 620 mg (0.61 mmol, 59%) of 12: mp 151–154 °C dec; IR (KBr) 3050, 2960, 2940, 2910, 2860, 1960 (br), 1890 (br), 1815 (br), 1590, 1572, 1480, 1433, 1310, 1290, 1200, 1180, 1090, 1025, 997, 738, 688, 500, 415 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.18 (30 H, br s), 2.45 (1 H, br t, $J = 16$ Hz), 2.28 (1 H, br t, $J = 16$ Hz), 2.0–1.0 (5 H, m), 0.90 (1 H, br d, $J = 8$ Hz). Anal. Calcd for $\text{C}_{43}\text{H}_{38}\text{PtBrIP}_2$: C, 50.70; H, 3.76. Found: C, 51.12; H, 3.79.

(2-Bromo-3-chlorobicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum (15). Compound 15 was prepared according to method A. A solution of 2-bromo-3-chlorobicyclo[2.2.1]hept-2-ene^{5a} (146.4 mg, 0.7 mmol) in 10 mL of freshly distilled tetrahydrofuran was added to tris(triphenylphosphine)platinum (500 mg, 0.5 mmol) under argon at 25 °C. The mixture was stirred for 18 h at ambient temperature and then concentrated in vacuo to a yellow oil, which was triturated with 25 mL of absolute ethanol to give 363 mg (0.39 mmol, 77%) of 15 as a white solid: mp 156–160 °C dec; IR (KBr) 3070, 3050, 2962, 2945, 2910, 2860, 1965 (br), 1895 (br), 1820 (br), 1590, 1575, 1480, 1433, 1310, 1290, 1218, 1182, 1118, 1092, 1025, 995, 798, 782, 738, 686, 630, 527, 511, 500, 413 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.15 (30 H, br s), 2.35 (1 H, br t, $J = 17$ Hz), 2.20 (1 H, br t, $J = 17$ Hz), 1.9–1.0 (5 H, m), 0.75 (1 H, br d, $J = 8$ Hz). An analytical sample was prepared via recrystallization from tetrahydrofuran-hexane: mp 174–185 °C dec. Anal. Calcd for $\text{C}_{43}\text{H}_{38}\text{PtBrClP}_2$: C, 55.70; H, 4.13. Found: C, 55.88; H, 4.25.

(2,3-Dichlorobicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum (16). Compound 16 was prepared according to method A. This provided 300 mg (0.34 mmol, 68%) of 16 as a white solid: mp 167–169 °C dec; IR (KBr) 3070, 3050, 2960, 2910, 2865, 1970 (br), 1900 (br), 1820 (br), 1680 (br), 1620 (br), 1590, 1575, 1480, 1437, 1310, 1290, 1195, 1182, 1117, 1092, 1025, 995, 812, 740, 690, 500, 418 cm^{-1} . This material dissociated

(35) Ugo, R.; Cariati, F.; La Monica, G. *Inorg. Synth.* 1968, 11, 105.

within 1 h in chloroform solution; attempted recrystallization of the material resulted in decomposition. Therefore, the crude product was submitted for analysis. Anal. Calcd for $C_{43}H_{38}PtCl_2P_2$: C, 58.51; H, 4.34; Cl, 8.03. Found: C, 57.92; H, 4.45; Cl, 7.72.

(2-Bromobicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum (17). Compound 17 was prepared according to method A. This provided 740 mg (0.83 mmol, 83%) of 17: mp 141–145 °C dec; IR (KBr) 3070, 3050, 2980, 2960, 2940, 2905, 2860, 1960 (br), 1900 (br), 1820 (br), 1588, 1570, 1480, 1435, 1315, 1292, 1245, 1185, 1092, 1070, 1030, 1000, 975, 912, 738, 720, 690, 592, 530, 500, 415 cm^{-1} . The olefin complex 17 was only sparingly soluble in common NMR solvents; this, combined with the ease of rearrangement of 17 to 35 in solution, did not permit the resolution of the Pt–H coupling constants in the NMR spectrum. Compound 17 was converted to its rearranged derivative 35 for elemental analysis.

(2-Chlorobicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum (18). Compound 18 was prepared according to method A. This provided 290 mg (0.34 mmol, 68%) of 18: mp 162–166 °C dec; IR (KBr) 3050, 2960, 2910, 2860, 1960 (br), 1895 (br), 1815 (br), 1680 (br), 1620 (br), 1585, 1475, 1432, 1310, 1290, 1245, 1182, 1115, 1090, 1025, 995, 980, 910, 740, 688, 495, 415 cm^{-1} . The instability of 18 in solution precluded its recrystallization, and a satisfactory elemental analysis was not obtained.

(Bicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum (19). Method C. A suspension of dibromobis(triphenylphosphine)platinum (1.0 g, 1.14 mmol) in 20 mL of absolute ethanol was treated with 2.5 mL of 95% hydrazine at 45 °C for 0.5 h. Bicyclo[2.2.1]hept-2-ene (0.49 g, 5.2 mmol) was added, and the mixture was stirred for 0.5 h at 45 °C. After being cooled to ambient temperature, the mixture was filtered and the precipitate was dried in vacuo. Recrystallization of this solid from methylene chloride–ethanol provided 190 mg (0.23 mmol, 21%) of 19: mp 140–145 °C dec; IR (KBr) 3060, 2950, 2860, 1970 (br), 1900 (br), 1820 (br), 1590, 1575, 1480, 1435, 1305, 1255, 1182, 1120, 1093, 1040, 1030, 1000, 900, 860, 845, 740, 690, 530, 505, 418 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.15 (30 H, br s), 2.30 (2 H, br t, $J = 65$ Hz), 2.20 (2 H, br m), 1.5–0.7 (5 H, m), 0.10 (1 H, br d, $J = 9$ Hz). Anal. Calcd for $C_{43}H_{40}PtP_2$: C, 63.46; H, 4.95. Found: C, 63.03; H, 4.96.

cis-Dibromobis(triphenylphosphine)platinum (33). Compound 33 was prepared according to a modification of the literature procedures.³⁶ A solution of tris(triphenylphosphine)platinum (5) (600 mg, 0.61 mmol) in 10 mL of dry toluene under argon was treated with 30 μ L of bromine. The orange color dissipated immediately, and a cream-colored solid was obtained. The mixture was filtered, and the precipitate was dried in vacuo for 24 h. Recrystallization of the crude product from hot chloroform–ethanol containing triphenylphosphine afforded 250 mg (0.28 mmol, 46%) of the cis isomer 33 as yellow crystals: mp 308–310 °C [lit.^{36b} mp 307–309 °C]; IR (KBr) 3050, 1940 (br), 1900 (br), 1820 (br), 1720 (br), 1587, 1565, 1480, 1433, 1310, 1190, 1160, 1117, 1090, 1025, 995, 740, 715, 690, 535, 510, 490 cm^{-1} . The cis isomer is differentiated from the trans isomer on the basis of the appearance of a peak at 535 cm^{-1} in the IR spectrum of the cis isomer.^{36b}

cis-Bis(triphenylphosphine)bromo(3-bromobicyclo[2.2.1]hept-2-en-2-yl)platinum(II) (32). A solution of 2,3-dibromobicyclo[2.2.1]hept-2-ene (100 mg, 0.4 mmol) in 2 mL of freshly distilled tetrahydrofuran under argon was cooled to –78 °C and treated with 230 μ L of 2.2 N *n*-butyllithium in hexane. After 1 h at –78 °C the solution was transferred via syringe to a suspension of cis-dibromobis(triphenylphosphine)platinum (300 mg, 0.34 mmol) in 10 mL of dry toluene under argon. After 2 h at room temperature, water was added and the layers were separated. The aqueous solution was extracted with three 20-mL portions of ether. The combined organic phases were dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude product was recrystallized from tetrahydrofuran–hexane to give 62 mg (0.06 mmol, 19%) of 32 as yellow crystals: mp 204–210 °C dec; IR (KBr) 3080, 3060, 2940, 2910, 2860, 1980 (br), 1900 (br), 1820 (br), 1590, 1578, 1487, 1440, 1190, 1160, 1095,

1030, 1020, 1000, 820, 742, 692, 542, 520, 495 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.50 (sh) and 7.15 (30 H, br s), 2.33 (2 H, 1:3:1 t, $J = 22$ Hz), 1.50 (sh) and 1.30 (4 H, br s), 0.38 (1 H, d, $J = 8$ Hz), –0.55 (1 H, d, $J = 8$ Hz). Anal. Calcd for $C_{43}H_{38}PtBr_2P_2$: C, 53.15; H, 3.94; Br, 16.45. Found: C, 52.99; H, 3.86; Br, 16.23.

trans-Bis(triphenylphosphine)bromo(3-bromobicyclo[2.2.1]hept-2-en-2-yl)platinum (31). A suspension of the platinum dibromobicyclo[2.2.1]hept-2-ene complex, 11, (1.00 g, 1.04 mmol) in 80 mL of absolute ethanol was heated at reflux for 1 h. The mixture was cooled to ambient temperature and filtered, and the precipitate was dried in vacuo over phosphorus pentoxide to give 0.66 g (0.66 mmol, 66%) of 31 as white crystals: mp 218–225 °C dec; IR (KBr) 3060, 2950, 2910, 2865, 1970 (br), 1895 (br), 1815 (br), 1590, 1575, 1482, 1435, 1310, 1285, 1178, 1160, 1095, 1025, 1000, 818, 740, 690, 505, 420 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.75 (12 H, br s), 7.35 (18 H, br s), 2.45 (1 H, br t, $J = 30$ Hz), 2.08 (1 H, br s), 0.83 (2 H, br d, $J = 8$ Hz), 0.10 (3 H, br unsym t, $J = 8$ Hz), –0.60 (1 H, br d, $J = 8$ Hz). An analytical sample was prepared via recrystallization from tetrahydrofuran–ethanol to give yellow crystals: mp 238–242 °C dec. Anal. Calcd for $C_{43}H_{38}PtBr_2P_2$: C, 53.15; H, 3.94; Br, 16.45. Found: C, 52.87; H, 3.97; Br, 16.27.

cis- and trans-Bis(triphenylphosphine)iido(3-bromobicyclo[2.2.1]hept-2-en-2-yl)platinum (13 and 14). A suspension of the platinum(0)–olefin complex 12 (0.69 g, 0.68 mmol) in 80 mL of absolute ethanol was refluxed for 1 h. The mixture was cooled to ambient temperature and filtered, and the solid was dried in vacuo over phosphorus pentoxide to give 350 mg (51%) of a mixture of 13 and 14 with 14 predominating (based on a comparison with the NMR spectra of the related platinum bromides 31 and 32): mp 205–210 °C dec. Fractional recrystallization of this mixture from methylene chloride–hexane gave a first crop of yellow crystals which appeared to be mainly the cis isomer 13: mp 210–220 °C dec; IR (KBr) 3075, 3050, 2940, 2850, 1480, 1432, 1310, 1280, 1180, 1150, 1088, 1020, 982, 735, 685, 500 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.6 (sh) and 7.20 (30 H, br m), 2.38 (2 H, br t, $J = 20$ Hz), 1.5–1.0 (4 H, m), 0.30 (1 H, br d, $J = 8$ Hz), –0.60 (1 H, br d, $J = 8$ Hz). Anal. Calcd for $C_{43}H_{38}PtP_2BrI$: C, 50.70; H, 3.76. Found: C, 50.20; H, 3.80.

The second crop appeared to be mainly the trans isomer 14 by NMR analysis, although some impurity apparently due to the cis isomer remained: mp 220–226 °C dec; IR (KBr) 3050, 2920, 2850, 1950 (br), 1890 (br), 1800 (br), 1720 (br), 1475, 1430, 1305, 1280, 1180, 1150, 1085, 1020, 992, 733, 680, 490 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.75 (12 H, br s), 7.35 (18 H, br s), 2.40 (1 H, br s), 2.10 (1 H, br s), 0.8 (2 H, br s), 0.15 (3 H, br s), –0.65 (1 H, br s). This material was not submitted for analysis; structural identification was based on comparison of its NMR spectrum with that of 31.

trans-Bis(triphenylphosphine)bromo(bicyclo[2.2.1]hept-2-en-2-yl)platinum (35). A suspension of the (bromobicyclo[2.2.1]hept-2-ene)platinum complex, 17, (520 mg, 0.58 mmol) in 65 mL of absolute ethanol was heated at reflux for 1 h. The mixture was filtered hot, and the mother liquor was allowed to cool slowly to ambient temperature as white crystals were deposited. The mixture was filtered, and the precipitate was dried in vacuo over phosphorus pentoxide to give 235 mg (0.26 mmol, 45%) of 35: mp 197–201 °C dec; IR (KBr) 3050, 2960, 2910, 2858, 1970 (br), 1890 (br), 1810 (br), 1590, 1575, 1480, 1435, 1310, 1292, 1185, 1158, 1093, 1030, 998, 790, 740, 688, 505, 420 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.70 (12 H, br s), 7.35 (18 H, br s), 4.85 (1 H, br t, $J = 38$ Hz), 2.45 (1 H, br t, $J = 25$ Hz), 1.92 (1 H, br s), 0.80 (2 H, br d, $J = 8$ Hz), 0.20 (2 H, br d, $J = 8$ Hz), –0.55 (2 H, br d, $J = 8$ Hz). Anal. Calcd for $C_{43}H_{38}PtBrP_2$: C, 57.85; H, 4.40; Br, 8.95. Found: C, 57.74; H, 4.48; Br, 9.08.

(3-Bromobicyclo[2.2.1]hept-2-en-2-yl)tris(triphenylphosphine)platinum Fluoroborate (36). A solution of the (3-bromobicyclo[2.2.1]hept-2-en-2-yl)platinum bromide, 31, (2.0 g, 2.1 mmol) in 35 mL of methylene chloride and 5 mL of acetone was treated with 450 mg of silver fluoroborate at 25 °C. The mixture was shaken briefly and then centrifuged. The supernatant was decanted and treated with a solution of triphenylphosphine (524 mg, 2 mmol) in 10 mL of methylene chloride. The solution was concentrated in vacuo, and the residue was taken up in methylene chloride. Addition of ether gave an insoluble inorganic impurity, which was discarded. The mother liquor was then treated with hexane until a precipitate appeared. The solid was

(36) (a) Lee, T. W.; Stoufer, R. C. *J. Am. Chem. Soc.* 1975, 97, 195. (b) Mastin, S. H. *Inorg. Chem.* 1974, 13, 1003.

collected, dried in vacuo, and recrystallized from chloroform-hexane to give 655 mg (0.5 mmol, 25%) of **36** as a yellow solid: mp 195–200 °C dec; IR (KBr) 3060, 2980, 2950, 2920, 2870, 1970 (br), 1900 (br), 1830 (br), 1630 (br), 1590, 1580, 1485, 1440, 1318, 1290, 1190, 1160, 1080 [very strong, $\nu_s(\text{BF}_4^-)$], 1000, 745, 690, 510, 415 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.20 (45 H, br s), 2.10 (1 H, br s), 1.75 (1 H, s), 0.85 (2 H, br s), 0.25 (3 H, br s), -0.55 (1 H, br d, $J = 8$ Hz); $^{13}\text{C NMR}$ (CDCl_3) 54.20, 53.32, 49.10, 27.71, 24.50 ppm (the 31 peak multiplet in the aromatic region has not been included in this listing); MS, m/e 981–982 [$\text{Pt}(\text{PPh}_3)_3^+$], 886–894 [$\text{Pt}(\text{PPh}_3)_2\text{C}_7\text{H}_8\text{Br}^+$], 715–725 [$\text{Pt}(\text{PPh}_3)_2^+$]. An analytical sample was prepared via recrystallization from chloroform-hexane; mp 210–213 °C dec. Anal. Calcd for $\text{C}_{61}\text{H}_{53}\text{PtF}_3\text{BrBF}_4 \cdot 2\text{CHCl}_3$: C, 51.14; H, 3.75. Found: C, 50.87; H, 3.78.

Reaction of 2-Bromo-3-iodobicyclo[2.2.1]hept-2-ene with Tris(triphenylphosphine)platinum and Sodium Amalgam. A flask containing 1.61 g (1.4 mmol) of 2% sodium amalgam was purged with argon and charged with a solution of tris(triphenylphosphine)platinum (**5**) (500 mg, 0.5 mmol) in 10 mL of freshly distilled tetrahydrofuran. The mixture was placed under positive pressure of argon, and 2-bromo-3-iodobicyclo[2.2.1]hept-2-ene (**8**) (210 mg, 0.7 mmol) in 2 mL of freshly distilled tetrahydrofuran was added. The mixture was stirred for 1.5 h at 25 °C and filtered under nitrogen pressure, and the filtrate was concentrated in vacuo. The residue was transferred to an inert-atmosphere drybox, and fractional crystallization with tetrahydrofuran-hexane was attempted. The crops of crystals were

analyzed by NMR spectroscopy: first crop (30 mg), **12**; second crop (29 mg), **14**; third crop (135 mg), mixture of **13** and **14**; and fourth crop (239 mg), **12**. The combined modes of trapping of 2-bromo-3-iodobicyclo[2.2.1]hept-2-ene by platinum thus amounted to 433 mg (0.43 mmol) of adducts, or 86%, based on **5**.

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Supplementary Material Available: Tables of bond lengths and bond angles, atomic coordinates and thermal parameters, and structure factor amplitude (19 pages). Ordering information is given on any current masthead page.

Approaching the σ^2, π Structural Limit of *s-cis* η^4 -Conjugated Diene Zirconocene Complexes

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(1,2,5,6-Tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane)zirconocene (**2a**), prepared by irradiation of diene **1a** and diphenylzirconocene, and (2,3-dimethylenebicyclo[2.2.1]heptane)zirconocene (**2b**), obtained by reduction of zirconocene dichloride with lithium in the presence of 2,3-dimethylenenorbornane (**1b**), both react with carbon monoxide under displacement of the conjugated diene forming zirconocene dicarbonyl. Envelope-shaped σ^2, π -type structures were found for the diene zirconocene units in X-ray diffraction studies of both complexes. **2a** crystallizes in space group $P\bar{1}$ ($Z = 4$) with cell constants $a = 8.578$ (2) Å, $b = 14.466$ (3) Å, $c = 15.717$ (1) Å, $\alpha = 75.00$ (1)°, $\beta = 88.566$ (8)°, and $\gamma = 89.12$ (2)° (7110 observed reflections, $R = 0.035$). Compound **2b** crystallizes in space group $P\bar{1}$ ($Z = 2$) with cell constants $a = 7.4540$ (7) Å, $b = 8.8377$ (8) Å, $c = 11.8934$ (7) Å, $\alpha = 84.704$ (5)°, $\beta = 88.922$ (5)°, and $\gamma = 79.765$ (7)° (3165 observed reflections, $R = 0.021$). Comparison of the molecular geometries of (diene)zirconocenes **2a, b, d, e** and the zirconocenes **3** reveals a continuously increasing metallacyclopentene character. In this series the reactivity of **2a** and **2b** toward carbon monoxide is markedly less influenced by ground-state effects as compared with that of **2d, 2e**, and **3**.

1,2,5,6-Tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane (**1a**) is a remarkable molecule, whose special features¹ have led to a broad exploration of its organic chemistry.² However, only a few attempts to coordinate this diene to a transition-metal center have become known.³ Structural properties of metal complexes of **1a** determined by X-ray diffraction methods, to our knowledge, have not been reported as yet.

We have recently prepared the bis(η -cyclopentadienyl)zirconium complex **2a** of the conjugated diene

1a.⁴ Among the known differently substituted (*s-cis*- η^4 -conjugated diene)zirconocenes⁵ (**2**, see Scheme I), **2a**

(1) Jorgensen, W. L.; Borden, W. T. *Tetrahedron Lett.* 1975, 226. Van Duijnen, P. T.; van der Ploeg, P.; Hogeveen, H.; Huurdeman, W. F. J. *Ibid.* 1975, 573. Hogeveen, H.; Huurdeman, W. F. J.; Kok, D. M. *J. Am. Chem. Soc.* 1978, 100, 871.

(2) Heldeweg, R. F.; Hogeveen, H. *J. Am. Chem. Soc.* 1976, 98, 2341. Hogeveen, H.; Huurdeman, W. F. J. *Ibid.* 1978, 100, 860. Heldeweg, R. F.; Hogeveen, H.; Schudde, E. P. *J. Org. Chem.* 1978, 43, 1912, 1916. Hogeveen, H.; Zwart, L. *Ibid.* 1979, 44, 1365. Hogeveen, H.; Elzinga, J. *Ibid.* 1979, 44, 2381 and references cited therein.

(3) (a) $\text{Fe}(\text{CO})_5$ complex: Elzinga, J.; Hogeveen, H. *Tetrahedron Lett.* 1976, 2383; *J. Org. Chem.* 1980, 45, 3957. (b) Ring-opening rearrangement occurs upon treatment with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$: Heldeweg, R. F.; Hogeveen, H. *J. Am. Chem. Soc.* 1976, 98, 6040.

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