process occurs giving benzaldehyde in a predicted yield of 250% (based on nitrate).

$$NO + {}^{1}/_{2}O_2 \rightarrow NO_2 \qquad (12)$$

$$6NO_2 + 8BF_3 \rightarrow 6NOBF_4 + {}^{3}/_{2}O_2 + B_2O_3 \qquad (13)$$

$$HNO + {}^{1}/_{2}O_2 \rightarrow HNO_2 \qquad (14)$$

Consistent with this explanation, the oxidation by the nitrate oxidants is catalytic, with respect to oxidant, in the presence of oxygen. The two catalytic reactions have similar rate profiles (Table III). Reactions at rates comparable to those observed for the stoichiometric oxidations ($\sim$8 mol PhCHO/mol oxidant^{-1}/h^{-1}) are observed for the first 10–15 min. Thereafter, the rates decrease and the final yields of $\sim$400% are obtained after 2 h.

Tovrog et al. reported that TPPCo(py)NO_2 disproportionated in the presence of $BF_3{\cdot}Et_2O$ to give the corresponding nitrosyl and nitrate complexes and that this mixture oxidized benzyl alcohol to benzaldehyde.[3] We reinvestigated the reaction and, once again, found no evidence for nitric or nitrous oxide by infrared spectroscopy.

In summary, displacement of X from $CpCo(S_2CNR_2)X$ is facile and dominates the reactions of the nitro and nitrato complexes with oxidizable organic substrates. Cationic phosphine complexes are obtained from **1b** and **1c** by reaction with triphenylphosphine, and the substrate is not oxidized. The redox reactions involving benzyl alcohol do not involve metal-bound nitrogen oxide ester intermediates but can be rationalized by schemes (e.g., Scheme I) based on the NO^+/HNO redox couple. Our results indicate that criteria for establishing oxidation by that redox couple are observation of (1) nitric and nitrous oxide products, (2) metal tetrafluoborate products without nitrogen oxide ligands, and (3) more than 1 equiv of product/mol of oxidant.

Registry No. **1a**, 87101-28-8; **1b**, 87101-30-2; **1c**, 87101-32-4; **2a**, 87101-27-7; **2b**, 87101-31-3; **2c**, 87101-33-5; **3a**, 87101-29-9; **3c**, 87101-34-6; **3d**, 87101-35-7; **4d**, 87101-37-9; (PPN)NO_2, 65300-05-2; (PPN)NO_3, 38011-35-7; $PhCH_2OH$, 100-51-6; PhCHO, 100-52-7.

Cumulenes as Ligands.[1] (η^2-Butatriene)platinum(0) Complexes, a New Structural Class of Cumulene Complexes

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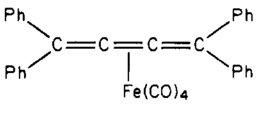
Received June 1, 1983

Displacement of ethylene from bis(triphenylphosphine)(ethylene)platinum(0) by four different butatrienes led to four new π complexes. In contrast to known butatriene complexes, the IR, ^{1}H NMR, and ^{31}P NMR spectra of these platinum compounds clearly show that the metal is bound to a terminal unsaturation of the triene. The π-bonding nature of the ligand attachment is indicated by the fast atom bombardment mass spectra and also ligand exchange reactions involving maleic anhydride. Attempts to produce binuclear platinum complexes were unsuccessful, but the platinum fragment may be replaced by rhodium upon reaction with Wilkinson's catalyst. These results are discussed in detail.

Olefin complexes comprise the oldest class of organometallic compounds, with the first reported olefin complex, Zeise's salt,[2] containing platinum. This metal has continued to be the most popular choice for producing π complexes.[3] Hartley has proposed a simple classification of olefin and acetylene π complexes,[4] with class S species modeled by the square-planar Zeise's salt and class T represented by the trigonal-planar compound bis(triphenylphosphine)(ethylene)platinum (**1**).

All of the known butatriene π complexes can be classified by using Hartley's scheme. For instance, the crystal structure of (tetraphenylbutatriene)tetracarbonyliron (**2**) reported by Bright and Mills[5] shows the trigonal-bipyramid coordination sphere of a typical pentacoordinate class T compound. West has reported the structure of a (diquinoethylene)rhodium complex (**3**)[6] that is in class S. We recently reported a crystal structure of a (butatriene)rhodium complex (**4**)[7] which also is a class S species.



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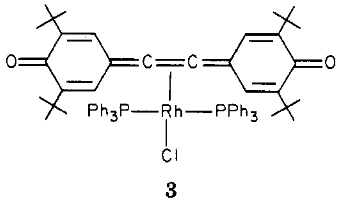

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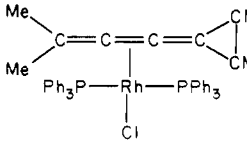

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(1) Third paper in a series. Part 2: White, M. R.; Stang, P. J. *Organometallics* **1983**, *2*, 0000. Abstracted in part from the Ph.D. dissertation of Mitchell R. White, The University of Utah, 1983.

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Table I. Properties of the (Butatriene)platinum Complexes 9-12

compd	yield,[a] %	mp,[b] °C	IR,[c] ν_{max} (cm^{-1})	^{1}H NMR,[d] δ (mult, H's)	^{13}C NMR,[h] δ
9	63	141-143	3050, 1935, 1595, 1480, 1435, 1095, 770, 745, 695	6.74-7.67 (complex m)	77.4, 124.1, 125.5, 127.4, 127.9, 128.0, 128.1, 128.3, 128.6, 128.8, 129.0, 129.5, 129.6, 129.8, 131.6, 132.5, 134.0, 134.2, 134.3, 134.5, 134.6, 134.7, 134.8, 134.9, 135.2, 139.1, 140.0, 146.6, 152.3
10	87	138-139	3050, 2910, 2860, 1925, 1595, 1480, 1435, 1095, 745, 695	0.57 (s, 6), 1.06 (s, 6), 6.75-7.57 (m, 40)	
11	60	79-81	3050, 2930, 2870, 1940, 1595, 1480, 1435, 1100, 750, 700	0.27 (q, 6),[e] 0.76 (t, 9),[e] 2.53 (s, 1),[f] 6.65-7.59 (m, 40)	5.1, 8.0, 109.2, 125.1, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8, 129.3, 129.5, 129.6, 130.9, 134.0, 134.1, 134.3, 134.4, 183.2
12[c]	75	94-96	3050, 2940, 2865, 1935, 1595, 1480, 1435, 1095, 745, 695	0.23-1.13 (m, 15), 2.83 (s, 0.5),[g] 6.22 (s, 0.5), 6.7-7.57 (m, 40)	

[a] Isolated yields. [b] All dec. [c] KBr pellet. [d] $CDCl_3$, Me_4Si internal standard. [e] J = 7 Hz. [f] J = 5 Hz. [g] J = 6 Hz. [h] $CDCl_3$.

Although these are the only reported X-ray structures of mononuclear butatriene π complexes, several other iron complexes have been published,[8] as well as our recent paper dealing with heterobimetallic (butatriene)rhodium complexes.[1] The iron species are all class T, while the rhodium ones are in class S.

The existence of stable (allene)platinum complexes[9] and the contrasting lack of known (butatriene)platinum compounds, along with our recent interest in (butatriene)-rhodium complexes, prompted us to investigate cumulenes as ligands on platinum. Using the Hartley classification as a guide, one would expect to find platinum(II) complexes in class S, with the platinum(0) compounds in class T. This report deals exclusively with the latter type.

Results and Discussion

One of the simplest entries into platinum(0) complexes of olefins is by olefin exchange, using **1** as starting material.[10] This procedure has been used to produce (allene)platinum(0) compounds,[10c] and the lack of interfering freed ligands after reaction makes this method very attractive. Indeed, stirring 1 equiv of tetraphenylbutatriene (**5**) with complex **1** for a few minutes in dichloromethane led to complete ligand exchange, and addition of methanol gave light yellow needle, crystals. Likewise the butatrienes **6–8** (Scheme I) produced three more complexes, all in good yields. Some of the properties of the product complexes **9–12** are given in Table I. All four compounds exhibit a relatively strong absorption in the region 1925–1940 cm^{-1}. The free butatrienes **6–8** exhibit a stretch at 2040–2060 cm^{-1},[11,12] and this absorption shifts to higher frequency upon complexation to rhodium.[1,7] The contrasting shift to lower frequency by complexation to platinum is indicative of an allene functionally in the product.

Table II. The ^{31}P NMR Properties of Complexes 9-12

compd	shift,[a] δ		$^2J_{P-P}$[b]	$^1J_{P-Pt}$[b]	
	P$_1$	P$_2$		P$_1$	P$_2$
9	28.77	26.21	37.1	3415.9	3664.3
10	28.55	25.48	23.0	2995.5	3549.7
11	32.00	26.10	34.8	3528.8	3584.4
12[c]	32.44	26.36	36.5	3471.2	3569.5
	20.36	17.84	10.8	2857.4	2451.4

[a] $CDCl_3$, relative to external 85% H_3PO_4. [b] Hertz. [c] Two isomers.

The ^{1}H NMR spectra of these complexes have some remarkable features. Compound **10** shows two sets of methyl peaks, each of six protons. The starting butatriene has only one absorption for the methyl substituents, at δ 1.33. Complex **11**, made from a butatriene that has a hydrogen substituent, shows a single-proton absorption at δ 2.53. This proton is found at δ 5.97 in the ^{1}H NMR spectrum of the free ligand. Complex **12** is apparently a mixture of two compounds, since the vinylic proton accounts for two peaks, at δ 6.22 and 2.83. Since the protons of ethylene are strongly shielded upon complexation to platinum(0),[13] the implication of the vinylic proton absorption in complex **11** is that the platinum is bound on the terminus of the triene linkage, as shown in Scheme I.

Complexation of a butatriene by a single metal center at a terminal unsaturation is completely unprecedented. Considering the propensity of platinum for insertion chemistry involving cyclopropane ring bonds[14] and group 4 metal–carbon bonds,[15] we felt that the information in the proton spectra might also be accommodated by alternative structures produced by oxidative addition reactions. To further ascertain the actual structure of these complexes, three more kinds of information were collected: fast atom bombardment (FAB) mass spectra,[16] ^{31}P NMR

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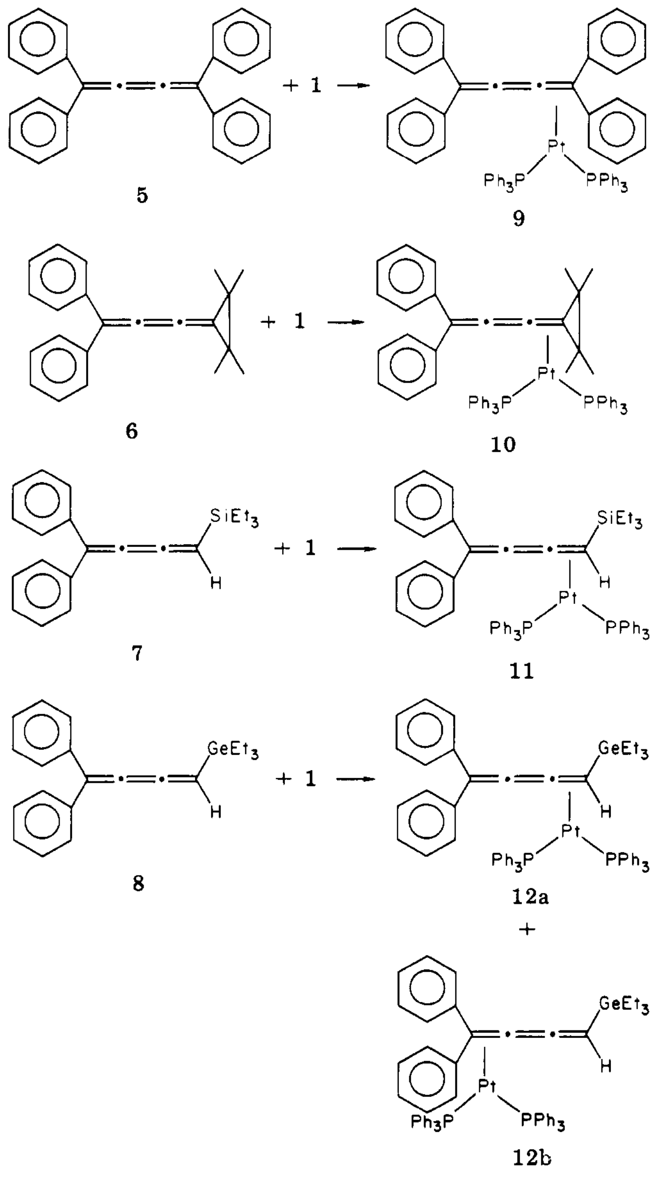
Scheme I. Pt Complexes



1 = $(Ph_3P)_2Pt(C_2H_4)$

spectra, and a ^{13}C NMR spectrum of complex **9** and **11**. The ^{31}P spectra are reported in Table II.

The FAB mass spectra of our (butatriene)rhodium complexes proved to be a valuable indicator of their π-complex nature.[1,7,17] In those compounds, only loss of the cumulene ligand as an intact unit was observed. For complexes **9**–**12**, again only loss of the complete butatriene is observed.[17] This argues against oxidative insertion of the platinum in complexes **10**–**12**, where such reaction might be expected. Further evidence for π complexation comes from ligand exchange reactions of these complexes with maleic anhydride. In each case, stirring the butatriene complex in CH_2Cl_2 with an equivalent of maleic anhydride leads to rapid and complete exchange of the cumulene; the freed ligand can be recovered by chromatography.

The ^{13}C NMR spectrum of tetraphenylbutatriene has an absorption at δ 152 which is assigned to the sp carbons.[18]

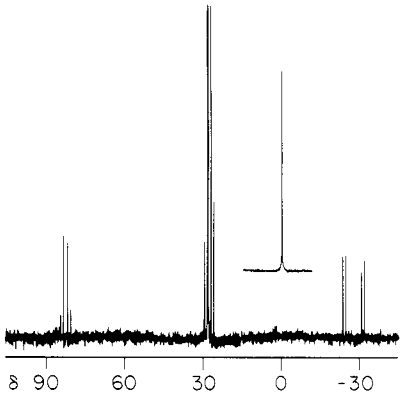


Figure 1. The ^{31}P NMR spectrum of complex **9**. Zero reference is 85% H_3PO_4.

Platinum is known to exert a strong shielding effect (40–70 ppm) on sp^2 carbons to which it is bound in π-complex fashion;[19] a similar effect would be expected for the sp carbons of a cumulene which is complexed. Indeed, such a shielding is noted in the (butatriene)rhodium complexes,[1,7] where both sp carbons are shifted into the region of the aromatic carbons of the phosphines. However, the ^{13}C NMR spectrum of **9** shows a clean, single peak at δ 152.3, indicating that at least one of the original sp carbons of the tetraphenylbutatriene ligand is not adjacent to platinum. Likewise, in uncomplexed cumulene **7** the two central sp carbons are at δ 170.8 and 163.7, where as in complex **11** only one sp carbon is observed at δ 183.2.

The ^{31}P NMR spectrum of complex **9** gives the clearest indication that the platinum is not centrally located on the unsaturated backbone. If the tetraphenylbutatriene had been symmetrically complexed, then the two phosphine ligands would be equivalent, leading to a simple, three-line spectrum—one phosphorus absorption, with two ^{195}Pt satellites, in a 1:4:1 relative intensity ratio. This is not the case, as shown in Table II and Figure 1. The figure gives the observed ^{31}P NMR spectrum of complex **9**, showing 12 lines. The four central lines comprise an AB spin system due to the two different phosphorous nuclei, and the eight smaller lines are from the ABX system which involves ^{195}Pt. The derived shifts and coupling constants are shown in Table II. Similarly, complexes **10** and **11** show 12-line spectra, and complex **12** shows a 24-line one. This last example comes from the superposition of two 12-line spectra, one for each isomer of the complex.

A summary of the spectral data thus gives the following structural details. The bis(triphenylphosphine)platinum fragment is π bound to one end of the butatriene linkage, a novel site selection in η^2-butatriene complexation. This mode of bonding leaves an allene functionality that manifests itself in the IR and ^{13}C NMR spectra. Complexes **9**–**12** are all Hartley class T species; the cumulene ligand axis is coplanar with the platinum coordination plane, since the two phoshorous nuclei are nonequivalent in each complex.

The justification of the unprecedented terminal olefin complexation in these complexes is quite straightforward. It is known that simple olefins π bound to platinum(0) are not free to rotate about the metal–olefin bond, even though they are usually held coplanar with the other ligands.[20] This experimental finding has been supported by molecular orbital arguments,[21] which show the rotation of such

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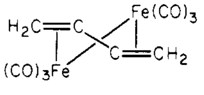
a ligand to involve an energy barrier which is comparable to the metal–olefin bond strength. This coplanarity requirement excludes binding of the platinum to the central olefin of the butatriene, since this olefin is coplanar with the four substituents of the cumulene. Any coplanar approach of the bis(triphenylphosphine)platinum fragment to the central unsaturation of tetraphenylbutatriene, for instance, leads to considerable steric interference between the phosphines and the in-plane phenyl rings on the approaching ligand, at distances too large for metal–olefin bonding. This is not the case in end-olefin complexation, where the ligand is rotated 90°, removing the phenyl groups from the phosphine exclusion cones.

Besides the ligand exchange reactions using maleic anhdyride, two other kinds of reactions were investigated by using these platinum complexes. Since binuclear iron complexes with a bridging cumulene ligand are known,[22] such as compound **13**, we felt that it might be possible to make binuclear platinum complexes. However, with use of 2 equiv of **1** and a butatriene such as **7**, only a 1:1 mixture of starting material and complex **11** was noted. Apparently after the first platinum fragment has complexed to the cumulene, the other terminus of the ligand becomes too sterically congested for a second attachment to occur.



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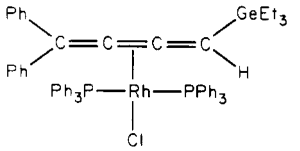

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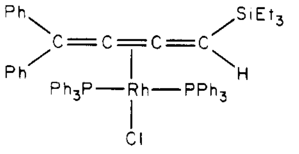

15

The second kind of reaction was to treat a platinum complex with an equivalent of Wilkinson's catalyst, chlorotris(triphenylphosphine)rhodium. In a typical experiment, complex **12** was allowed to react with Wilkinson's catalyst in benzene for 2 h, at which time the solution had become homogeneous and was a light yellow-orange color. Thin-layer chromatography indicated the presence of a (butatriene)rhodium complex, **14**, which we have reported earlier.[1] Chromatography as previously described yielded the rhodium species, which was identical with authentic material. A similar reaction using **11** gave the analogous rhodium complex **15**. This constitutes the first report of a cumulene ligand transfer from one metal to another and undoubtedly occurs because the platinum moiety is not attached at the most electron-poor site of the butatriene ligand, while the rhodium fragment is. Whether this transfer occurs due to the presence of trace quantities of freed ligand, by preassociation or through some heterobimetallic (rhodium–platinum) complex association remains to be determined.

In summary, we have demonstrated a simple, high-yield method for the generation of (butatriene)platinum(0) complexes and shown that these compounds are of a new structural class, namely, the terminally bound cumulene complexes. Since such structures are unique in the field of cumulene π complexes, we are further pursuing the chemical and structural features of these materials, which will be the subject of future reports.

Experimental Section

General Data. Melting points were recorded on a Mel-Temp capillary apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer. The ^{1}H NMR spectra were recorded on a Varian EM-390 or FT-80A spectrometer, and the ^{1}P NMR spectra were taken on a Varian FT-80A. The ^{13}C NMR spectra were recorded on a Varian SC-300 spectrometer. The FAB mass spectra were recorded on a Varian MAT 731 spectrometer fitted with an Iontech FAB source.

Materials. All commercial reagents were ACS reagent grade. Solvents were purified and rigorously dried immediately prior to use. Bis(triphenylphosphine)(ethylene)platinum was prepared in two steps from tetrakis(triphenylphosphine)platinum (Strem Chemicals), according to the procedure of Cook and Jauhal.[13]

Tetraphenylbutatriene (5). This cumulene was prepared in three steps according to the procedure of Sisenwine and Day,[23] in 37.7% overall yield, mp 234–235 °C (lit.[23] mp 235–236 °C).

1,1,2,2-Tetramethyl-3-(3,3-diphenyl-1,2-propadienylidene)cyclopropane (6). This compound was prepared according to the procedure of Stang and Fisk[11] and purified by chromatography (unactivated silica, hexanes) immediately prior to use.

4,4-Diphenyl-1-(triethylsilyl)-1,2,3-butatriene (7) and 4,4-Diphenyl-1-(triethylgermyl)-1,2,3-butatriene (8). These two cumulenes were prepared according to the procedure of Stang and White[12] and purified by chromatography (unactivated silica, hexanes) immediately prior to use.

General Procedure for the Formation of Platinum(0) Complexes of Butatrienes. Bis(triphenylphoshine)(η^2-tetraphenylbutatriene)platinum (9). A 50-mL three-neck round-bottom flask was fitted with an argon inlet, bubbler, and magnetic stirring, and then 35.6 mg (100 μmol) of tetraphenylbutatriene in 10 mL of dichloromethane was introduced and the system flushed with argon. Bis(triphenylphosphine)(ethylene)platinum (74.7 mg, 100 μmol) was added, and an immediate lightening of the color from bright yellow was noted, as well as an indication of gas evolution. The mixture was stirred for a further 15 min, and then methanol was added dropwise. As soon as cloudiness become apparent, the mixture was allowed to stand at −10 °C overnight. The crystals were collected, washed with a small portion of cold methanol (−30 °C), and air-dried, giving 68 mg (63%) of very fine, slightly yellow needles, mp 141–143 °C dec. Anal. Calcd for $C_{64}H_{50}P_2Pt$: C, 71.43; H, 4.68; P, 5.76. Found: C, 70.99; H, 4.86; P, 5.38.

Bis(triphenylphosphine)[η^2-1,1,2,2-tetramethyl-3-(3,3-diphenyl-1,2-propadienylidene)cyclopropane]platinum (10). This complex was prepared according to the general procedure from 74.7 mg (100 μmol) of **1** and 28.6 mg (100 μmol) of **6**, giving 87 mg (86%) of light yellow needles, mp 138–139 °C dec. Anal. Calcd for $C_{58}H_{52}P_2Pt$: C, 69.24; H, 5.21, P, 6.16. Found: C, 69.50; H, 5.45; P, 6.47.

Bis(triphenylphosphine)[η^2-4,4-diphenyl-1-(triethylsilyl)-1,2,3-butatriene]platinum (11). This compound was prepared according to the general procedure from 74.7 mg (100 μmol) of **1** and 31.9 mg (100 μmol) of **7**, giving 62 mg (60%) of fine yellow needles, mp 79–81 °C dec. Anal. Calcd for $C_{58}H_{56}P_2PtSi$: C, 67.10; H, 5.44; P, 5.97. Found: C, 66.43; H, 5.52; P, 6.05.

Bis(triphenylphosphine)[4,4-diphenyl-1-(triethylgermyl)-1,2,3-butatriene]platinum (12). This complex was prepared according to the general procedure from 74.7 mg (100 μmol) of **1** and 36.3 mg (100 μmol) of **8**, yielding 81 mg (75%) of yellow-orange crystals, mp 94–96 °C dec. Anal. Calcd for $C_{58}H_{56}GeP_2Pt$: C, 64.34; H, 5.21; P, 5.72. Found: C, 64.17; H, 5.14; P, 5.88.

Ligand Exchange Reactions Using Maleic Anhydride. In a typical reaction, 21.6 mg (20 μmol) of complex **12** and 2 mg (20 μmol) of maleic anhydride were placed in a 25-mL stoppered Erlenmeyer flask. The flask was flushed with argon, and 10 mL

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of degassed chloromethane was added by syringe. The mixture was stirred magnetically for 2 min and then stopped. An IR spectrum taken at this point showed the presence of the characteristic cumulenic absorption of the ligand **8** near 2050 cm^{-1} and the absence of the allenic absorption due to the complex (Table I). After removal of solvent and chromatography (unactivated silica, hexanes), 5.2 mg of butatriene **8** was recovered (72%). similar reactions using the other platinum complexes gave good yields of recovered butatrienes.

Attempted Binuclear Platinum Complexes. In a typical reaction, 37.4 mg (50 μmol) of complex **1** was allowed to react with 9.1 mg (25 μmol) of cumulene **8** in dichloromethane at room temperature for 1 h. The solvent was removed and the residue analyzed by IR and ^{1}H NMR, which indicated the presence of both **1** and **12**. Refluxing in benzene gave no change at short reaction times but led to destruction of the material at longer times. Similar reactions using **6** and **7** also gave no indication of the presence of binuclear species but rather mixtures of mononuclear complex and starting material.

Metal Exchange Reactions. Wilkinson's catalyst (9.3 mg, 10 μmol) and **12** (10.8 mg, 10 μmol) were stirred in 10 mL of benzene at ambient temperature for 2 h. The initially heterogeneous reaction mixture slowly became clear, with a residual yellow-orange color. Removal of the benzene and chromatography gave 7.4 mg of complex **14**, identical with authentic material by melting point and IR and ^{1}H NMR spectra. Similarly, complex **11** gave the rhodium compound **15**.

Acknowledgment. This research was supported by the NSF (Grant CHE 81-03596).

Registry No. 1, 12120-15-9; **5**, 1483-68-7; **6**, 75144-31-9; **7**, 86374-30-3; **8**, 79073-90-8; **9**, 87190-02-1; **10**, 87190-03-2; **11**, 87206-72-2; **12a**, 87190-04-3; **14**, 87247-40-3; **15**, 87247-41-4; chlorotris(triphenylphosphine)rhodium, 14694-95-2; maleic anhydride, 108-31-6; **12b**, 87190-05-4.

Reaction of (π-Allyl)palladium Complexes from Allene with Nucleophiles. Synthesis of Conjugated Exocyclic Dienes

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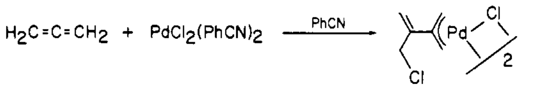
Received June 15, 1983

Allene reacts with palladium chloride to produce a (π-allyl)palladium complex (**1**) containing two allene units connected at their central carbons. This complex reacts with bifunctional nucleophiles such as dimethyl malonate, phenyl cyanomethyl sulfone, *n*-butylamine, and dimethylhydrazine to produce exocyclic dienes **2**, **4**, **7**, and **8** in fair yields, in a process which involves nucleophilic attack at the allylic chloride position followed by attack at a π-allyl terminus. The dianions of acetylacetone, ethyl acetoacetate, and dimethyl succinate were much less efficient in this reaction, giving cyclic material in only low yield.

Introduction

Reaction of allene with dichlorobis(benzonitrile)palladium(II) in benzonitrile produces a high yield of a (π-allyl)palladium complex containing two allene units connected at their central carbons (eq 1).[1-3] Early studies



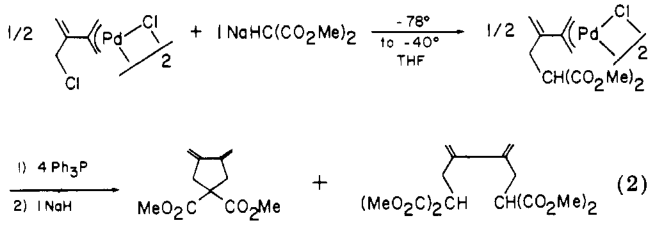
(1)

1

with this complex revealed that the bridging chlorides could be exchanged for bromide, iodide, thiocyanate, or acetylacetone and that the complex reacted reversibly with ammonia, pyridine, or *p*-toluidine in a bridge-splitting reaction.[4] In the intervening years, the chemistry of (π-allyl)palladium complexes has been extensively developed, with particular attention to their reactions with nucleophiles.[5-8] Complex **1** is interesting in this regard in that it has two sites available for nucleophilic attack, the allylic chloride and the π-allyl ligand. Herein we report the reactions of complex **1** with bifunctional nucleophiles to produce conjugated exocyclic dienes.

Results and Discussion

Initial studies focussed on the use of dimethyl malonate as the nucleophile. Since (π-allyl)palladium complexes ostensibly do not react with nucleophiles in the absence of added ligands,[8] it was reasoned that reaction of complex **1** with the anion of dimethyl malonate in the absence of added ligands should result in exclusive displacement of the allylic chloride. Subsequent addition of a phosphine ligand (to permit reaction at the π-allyl position) and base (to generate the anion) should permit ring closure generating the desired exocyclic diene **2** (eq 2). Indeed, carrying



(2)

2 3

out this reaction as in eq 2 resulted in a 54% isolated yield of the desired product **2**, along with varying amounts of the bis adduct **3**. Regardless of reaction conditions bis

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