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Chelating P,N versus P,P Ligands: Differing Reactivity of Donor-Stabilized Pt(η^2-PhC≡CPh) Complexes Toward Diphenylacetylene

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The thermal activation of the η^2-diphenylacetylene complex (PN)Pt(η^2-PhC≡CPh) (**1**) (PN = (diisopropylphosphinodimethylamino)ethane leads to the formation of the platinacyclopenta-2,4-diene compound (PN)Pt$(CPh)_4$ (**3**), which can be quantitatively obtained by reaction of **1** with 1 equiv of diphenylacetylene. Two transient intermediates are observed by ^{31}P NMR spectroscopy during the course of the latter reaction. These species were independently synthesized and characterized. Hexaphenylbenzene is catalytically generated by reaction of **1** in the presence of excess diphenylacetylene. In contrast, no reaction of diphenylacetylene with (dippe)Pt(η^2-PhC≡CPh) (**2**) (dippe = bis(diisopropylphosphino)ethane) was observed.

Introduction

Alkyne complexes of late transition metals play an important role in the cyclotrimerization reaction of acetylenes to benzene derivatives.[1] Generally, the insertion of an alkyne into the M−η^2-acetylene bond initially leads to a metalacyclopenta-2,4-diene and subsequently to larger metalacyclic complexes and benzene derivatives, respectively. This reaction is known for many compounds of d^8−d^{10} metals, such as Fe, Co, Ni, Ru, Rh, Pd, and Ir.[2] However, insertion reactions in corresponding Pt(0)−alkyne complexes are much less common but have been reported in a few cases.[3]

Zerovalent Pt complexes are typically isolated with ligands such as phosphines,[4] imines,[5] amides,[6] isonitriles,[7b,c] olefins,[4c,8] or alkynes.[7] These systems not only act as good σ-donors but provide considerable π-acceptor capabilities to stabilize the electron-rich metal center. However, much less attention has been paid to bidentate mixed donor systems as ligands for late transition metal alkyne complexes. We have recently reported on the synthesis of the Pt(0)−diphenylacetylene complex (PN)-Pt(η^2-PhC≡CPh) (**1**) bearing a hemilabile P,N-hybrid ligand (PN = (diisopropylphosphinodimethylamino)-ethane).[9] Because the dimethylamino group lacks in π-acceptor capability, the coordinative M−NR_2 bond is considered to be labile.[10] This situation should lead not only to an intrinsic instability of the (PN)Pt(η^2-alkyne) complex but also to an enhanced reactivity of the metal center toward substrates.

We report here on the thermal activation of (PN)Pt-(η^2-PhC≡CPh) and on the reductive coupling reaction of diphenylacetylene with the Pt−η^2-alkyne bond. A comparison with the system (dippe)Pt(η^2-PhC≡CPh) (dippe = bis(diisopropylphosphino)ethane), which contains a chelating bisphosphino ligand, was carried out.

Results and Discussion

Preparation and Characterization of Donor-Stabilized Pt(η^2-PhC≡CPh) Complexes. Reaction of

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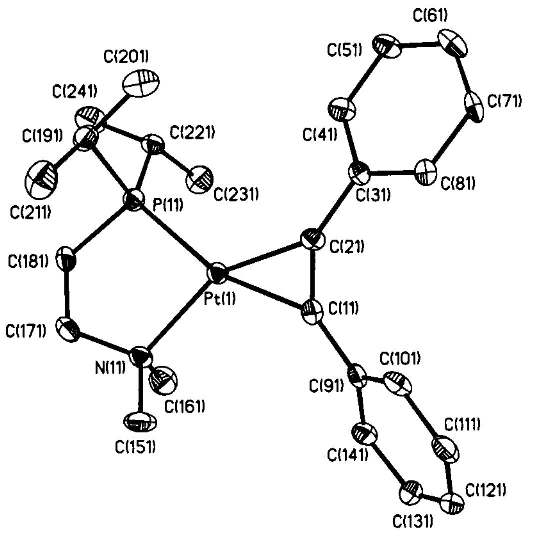
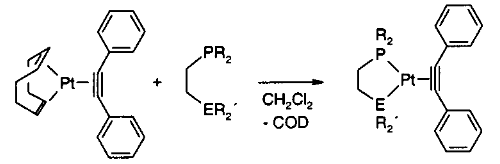


Figure 1. Molecular structure of (PN)Pt(PhC≡CPh) (**1**) (ORTEP diagram; 30% probability ellipsoids).

(COD)Pt(η^2-PhC≡CPh)[7b] with 1 equiv of PN[11] or dippe[12] afforded the η^2-diphenylacetylene complexes (PN)Pt(η^2-PhC≡CPh) (**1**) and (dippe)Pt(η^2-PhC≡CPh) (**2**), respectively (eq 1). These compounds were obtained as orange, air- and moisture-sensitive solids in high yields, and their synthesis has recently been described in detail.[9] **1** and **2** have been further characterized by single-crystal X-ray diffraction. The molecular structures of **1** and **2** are illustrated in Figures 1 and 2, and selected bond lengths and angles are listed in Tables 1 and 2, respectively. The structural analyses revealed the expected distorted square-planar geometry at the metal center with the alkyne ligand in the P−Pt−N and P−Pt−P plane. The elongated C≡C bonds and the bending of the C≡C−C angles compared to free diphenylacetylene[13] reflect major contribution of π^* back-donation.[2c,7b,14] The C−C triple bond distances and bending angles are similar to those reported for $(PPh_3)_2$-Pt(η^2-PhC≡CPh).[15]



(1)

E = N, R = iPr, R´= Me: **1**
E = P, R = R´= iPr: **2**

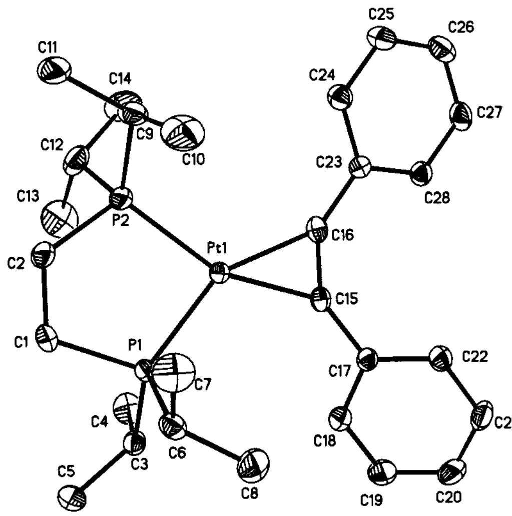


Figure 2. Molecular structure of (dippe)Pt(PhC≡CPh) (**2**) (ORTEP diagram; 30% probability ellipsoids).

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

	Bond Lengths		
Pt(1)−N(11)	2.221(8)	C(11)−C(21)	1.312(13)
Pt(1)−P(11)	2.247(2)	C(21)−C(31)	1.458(13)
Pt(1)−C(11)	2.054(9)	C(11)−C(91)	1.443(13)
Pt(1)−C(21)	1.994(9)		
	Bond Angles		
C(21)−Pt(1)−C(11)	37.8(4)	Pt(1)−P(11)−C(181)	104.1(3)
C(21)−Pt(1)−P(11)	123.6(3)	Pt(1)−N(11)−C(171)	111.0(6)
C(11)−Pt(1)−N(11)	114.3(3)	C(21)−C(11)−C(91)	142.7(9)
N(11)−Pt(1)−P(11)	84.3(2)	C(11)−C(21)−C(31)	143.3(9)

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2

	Bond Lengths		
Pt(1)−P(1)	2.2577(9)	C(15)−C(16)	1.301(5)
Pt(2)−P(2)	2.2672(10)	C(15)−C(17)	1.464(5)
Pt(1)−C(15)	2.029(3)	C(16)−C(23)	1.452(4)
Pt(1)−C(16)	2.047(3)		
	Bond Angles		
C(15)−Pt(1)−C(16)	37.24(13)	C(2)−P(2)−Pt(1)	108.76(12)
C(15)−Pt(1)−P(1)	158.28(10)	P(1)−Pt(1)−P(2)	86.84(3)
C(16)−Pt(1)−P(2)	121.05(10)	C(15)−C(16)−C(23)	140.7(3)
C(1)−P(1)−Pt(1)	109.72(12)	C(16)−C(15)−C(17)	144.4(3)

Thermal Activation Reactions of 1 and 2. We have recently shown that **1** and **2** undergo migration of the metal center with subsequent insertion into the C−Ph bond upon irradiation with UV light.[9] We were also interested in the reactivity of the η^2-diphenylacetylene complexes under thermal conditions. A solution of **1** in C_6D_6 was heated to $T = 70$ °C, and the reaction was monitored by ^{31}P NMR spectroscopy. Within 3 days the starting material was quantitatively consumed while a major species was formed in ~50% spectroscopic yield. This compound **3** was obtained as a colorless solid after recrystallization from pentane/CH_2Cl_2 at $T = -30$ °C. The $^{31}P\{^1H\}$ NMR spectrum of **3** showed a singlet at $\delta = 52.8$ ppm with Pt satellites ($^1J_{Pt-P} = 2228$ Hz). The significantly smaller coupling constant compared to the starting material ($^1J_{Pt-P} = 3647$ Hz) implies substituents σ-bonded to the Pt center. In the ^{1}H NMR

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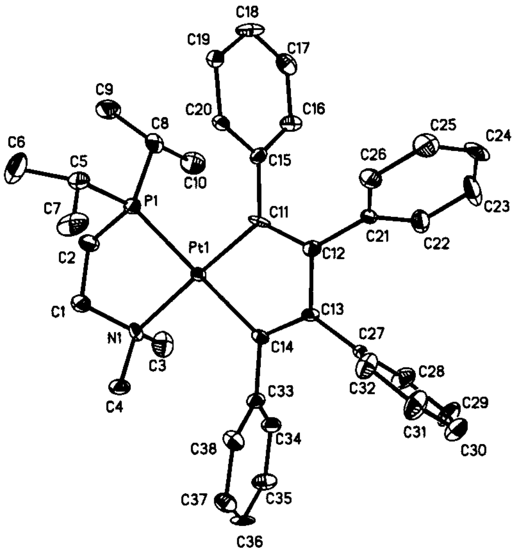


Figure 3. Molecular structure of (PN)Pt(CPh)$_4$ (**3**) (ORTEP diagram; 30% probability ellipsoids).

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

	Bond Lengths		
Pt(1)−N(1)	2.273(9)	C(13)−C(14)	1.350(16)
Pt(1)−P(1)	2.291(4)	C(14)−C(33)	1.477(17)
Pt(1)−C(14)	2.078(12)	C(13)−C(27)	1.465(15)
Pt(1)−C(11)	1.982(12)	C(12)−C(21)	1.504(15)
C(11)−C(12)	1.389(17)	C(11)−C(15)	1.478(17)
C(12)−C(13)	1.488(16)		
	Bond Angles		
N(1)−Pt(1)−P(1)	82.7(3)	C(13)−C(14)−Pt(1)	114.2(8)
C(14)−Pt(1)−C(11)	80.6(5)	C(14)−Pt(1)−N(1)	98.8(4)
Pt(1)−C(11)−C(12)	116.0(8)	C(11)−Pt(1)−P(1)	98.0(4)
C(11)−C(12)−C(13)	114.4(10)	Pt(1)−N(1)−C(1)	111.3(7)
C(12)−C(13)−C(14)	114.8(10)	Pt(1)−P(1)−C(2)	103.4(5)

spectrum resonances were observed for four unique phenyl groups. In particular, four sets of *ortho*-phenyl protons were detected. A crystal of **3** suitable for X-ray diffraction was obtained by slow recrystallization from pentane/CH$_2$Cl$_2$ at $T = -30$ °C. The molecular structure of **3** is illustrated in Figure 3, and selected bond lengths and angles are listed in Table 3. The structural analysis revealed that **3** is the platinacycle (PN)Pt(CPh)$_4$. The C−C distances C(11)−C(12) and C(13)−C(14) are 1.389(17) and 1.350(16) Å and therefore very similar to the value of 1.337(6) Å for a simple C=C double bond.[16] However, the bond length C(12)−C(13) of 1.488(16) Å is indicative of a single bond between two double bonds.[16] These values suggest that the platinacycle **3** has a localized double-bond system and is best described as a platinacyclopenta-2,4-diene complex. The formation of **3** by thermolysis of **1** is only possible if compound **1** partially decomposes to provide free diphenylacetylene. To show whether this phenomenon is due to the intrinsic instability of **1**, a solution of **2** in C$_6$D$_6$ was heated to $T = 70$ °C and monitored by ^{31}P NMR spectroscopy. Interestingly, the η^2-diphenylacetylene complex **2**, which contains the chelating bisphosphino ligand dippe, does not lead to a metalacyclic product. Even at prolonged heating at $T = 100$ °C no reaction or decomposition of **2** was observed.

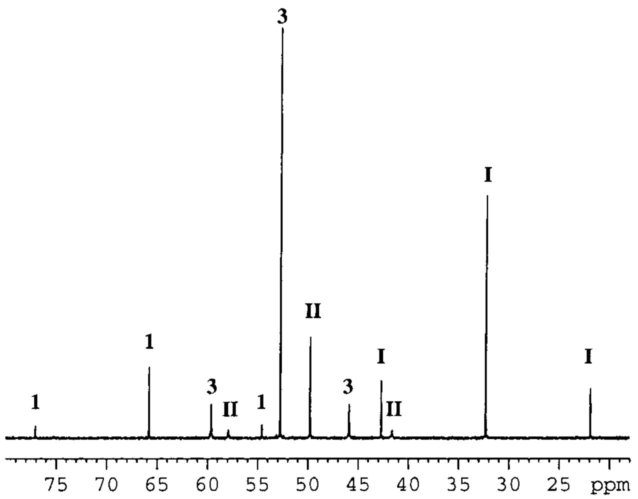
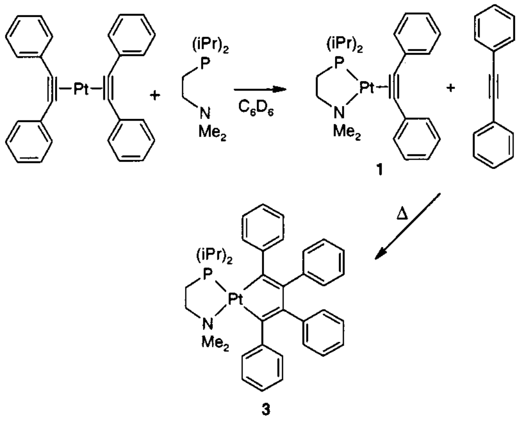


Figure 4. ^{31}P NMR spectrum (162 MHz) of the reaction of **1** with diphenylacetylene at $t = 23$ h ($T = 78$ °C).

Scheme 1



Stimulated by these observations, we were interested in the thermolysis of **1** in the presence of 1 equiv of diphenylacetylene. We found that a 1:1 mixture of **1** and diphenylacetylene can easily be generated in situ by reaction of Pt(η^2-PhC≡CPh)$_2$[7a,b] with 1 equiv of the P,N ligand in C$_6$D$_6$ according to Scheme 1. The orange solution was heated to $T = 100$ °C and monitored by ^{31}P NMR spectroscopy. The starting material was indeed quantitatively converted to **3** within 42 h. Surprisingly, two transient intermediates were observed during the course of the reaction. The ^{31}P NMR spectrum recorded after $t = 23$ h (reaction temperature $T = 78$ °C) is illustrated in Figure 4. A singlet at $\delta = 32.3$ ppm with Pt satellites ($^1J_{\text{Pt-P}} = 3336$ Hz) was observed for intermediate **I**, while a singlet at $\delta = 49.8$ ppm with broad Pt satellites ($^1J_{\text{Pt-P}} = 2608$ Hz) was detected for intermediate **II**. Again, the smaller Pt−P coupling constant of intermediate **II** compared to an η^2-alkyne complex suggests the presence of substituents σ-bonded to the metal center. We were able to synthesize and characterize **I** and **II** independently; reaction of (COD)Pt(η^2-PhC≡CPh) with 2 equiv of the P,N ligand in C$_6$D$_6$ led to the formation of the bisphosphino complex (NP)$_2$Pt(η^2-PhC≡CPh) (**4**), which was quantitatively

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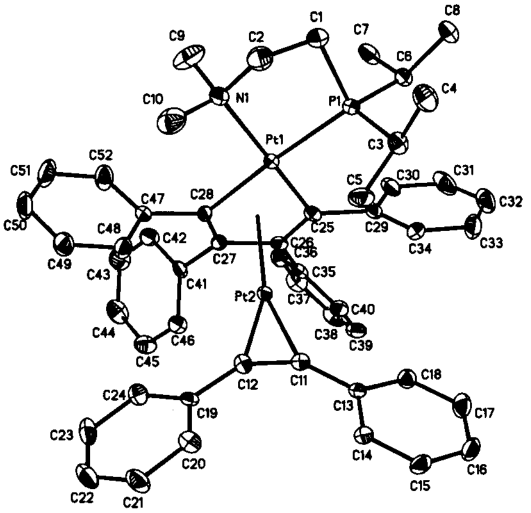
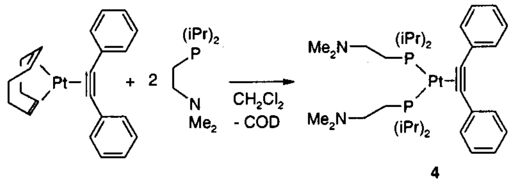


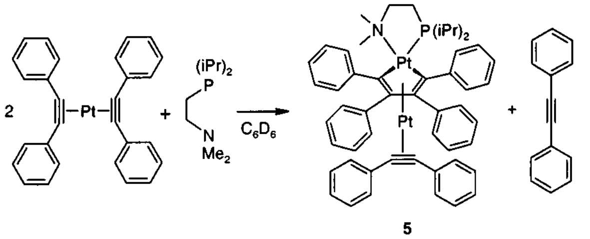
Figure 5. Molecular structure of (PN)Pt(CPh)$_4$Pt(η^2-PhC≡CPh) (**5**) (ORTEP diagram; 30% probability ellipsoids).

obtained as a yellow, air- and moisture-sensitive oil (eq 2). **4** was characterized by ^{1}H and ^{31}P NMR spectroscopy as well as elemental analysis.



(2)

The ^{31}P NMR data of **4** are identical with those observed for intermediate **I**. In complex **4** the two P,N molecules act as monodentate ligands with coordination to the metal center via the diisopropylphosphino group. Intermediate **II**, however, was synthesized by reaction of 2 equiv of Pt(η^2-PhC≡CPh)$_2$ with 1 equiv of the P,N ligand at T = 70 °C in C$_6$D$_6$ (eq 3). The product **5** with identical ^{1}H and ^{31}P NMR data as intermediate **II** was isolated as a dark red solid from the reaction mixture in 68% yield.



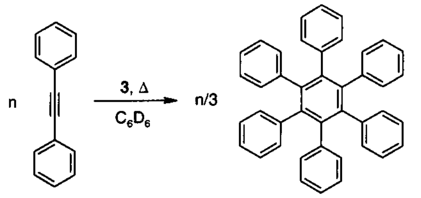
(3)

Crystals suitable for X-ray diffraction were obtained after recrystallization from C$_6$D$_6$/pentane at room temperature. The molecular structure of **5** is illustrated in Figure 5, and selected bond lengths, distances, and angles are listed in Table 4. The structural analysis revealed that the intermediate **II** (**5**) is a platinacyclopenta-2,4-diene complex of Pt(0). The Pt(0)−diphenylacetylene fragment is η^4-coordinated to the metalacycle in a half-sandwich fashion. On complexation, the bond distances C(25)−C(26) and C(27)−C(28) in the metalacycle are slightly elongated by approximately 0.03 Å compared to the C=C double bonds in the free platinacyclopenta-2,5-diene system. The Pt(1)−Pt(2) distance of 3.064 Å is considered to be too long for a bonding interaction. To the best of our knowledge, this structural motif of a Pt(0) complex has not been reported in the literature so far. However, a related dinuclear Ni(0)/Ni(II) complex was described by Pörschke. In this compound, an ethyne ligand bridges the metal centers of a donor-stabilized nickelacyclopenta-μ-2,4-diene complex and a (dippe)Ni(0) fragment.[17]

Table 4. Selected Bond Lengths (Å), Distances (Å), and Bond Angles (deg) for 5

Bond Lengths/Distances			
Pt(1)−N(1)	2.245(5)	Pt(1)···Pt(2)	3.0640(3)
Pt(1)−P(2)	2.2908(15)	Pt(2)−C(25)	2.359(5)
Pt(1)−C(25)	2.023(6)	Pt(2)−C(26)	2.222(5)
Pt(1)−C(28)	2.098(6)	Pt(2)−C(27)	2.241(5)
C(25)−C(26)	1.422(7)	Pt(2)−C(28)	2.361(5)
C(26)−C(27)	1.494(8)	Pt(2)−C(11)	2.008(6)
C(27)−C(28)	1.381(8)	Pt(2)−C(12)	1.995(6)
		C(11)−C(12)	1.294(8)
Bond Angles			
P(1)−Pt(1)−N(1)	82.05(14)	Pt(1)−C(25)−C(26)	117.1(4)
C(25)−Pt(1)−C(28)	78.0(2)	C(25)−C(26)−C(27)	112.7(5)
C(25)−Pt(1)−P(1)	99.39(16)	C(26)−C(27)−C(28)	113.5(5)
C(28)−Pt(1)−N(1)	100.7(2)	C(11)−Pt(2)−C(12)	37.7(2)
Pt(1)−N(1)−C(2)	111.7(4)	C(13)−C(11)−C(12)	145.3(6)
Pt(1)−P(1)−C(1)	103.9(2)	C(11)−C(12)−C(19)	147.0(6)
Pt(1)−C(28)−C(27)	115.6(4)		

The platinacyclopenta-2,4-diene complex **3** turned out to be an intermediate in the catalytic formation of hexaphenylbenzene by (PN)Pt(η^2-PhC≡CPh) (eq 4). A solution of (PN)Pt(η^2-PhC≡CPh) and excess diphenylacetylene in C$_6$D$_6$ was heated at T = 100 °C and monitored by ^{1}H and ^{31}P NMR spectroscopy.



(4)

Initially, the quantiative formation of the platinacyclopenta-2,4-diene complex was observed. Hexaphenylbenzene was then catalytically generated, although this reaction turned out to be very slow (1 turnover/20 days). However, once quantitatively formed, **3** remained the only intermediate observed by ^{31}P NMR spectroscopy during the course of the catalytical reaction.

In contrast to the results mentioned above, insertion reactions of diphenylacetylene into the Pt−alkyne bond in (dippe)Pt(η^2-PhC≡CPh) (**2**) were not observed. Heating a solution of **2** plus diphenylacetylene at T = 100 °C for 6 days showed no change in the ^{1}H and ^{31}P NMR spectra.

Mechanistic Considerations. We assume that the initial step in the formation of the metallacycle **3** is the displacement of the amino group by a second alkyne with subsequent C−C coupling and recoordination of the nitrogen donor to the metal center (Scheme 2). This assumption is based on the fact that compound **2**, containing two strong σ-donor as well as strong π-acceptor phosphorus ligands, does not react with diphen-

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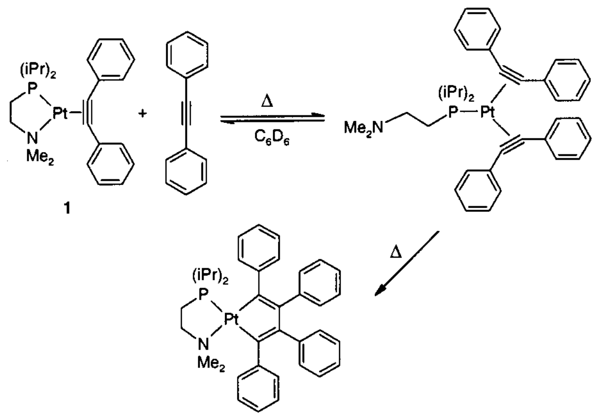
[17] Pörschke, K.-R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1288.

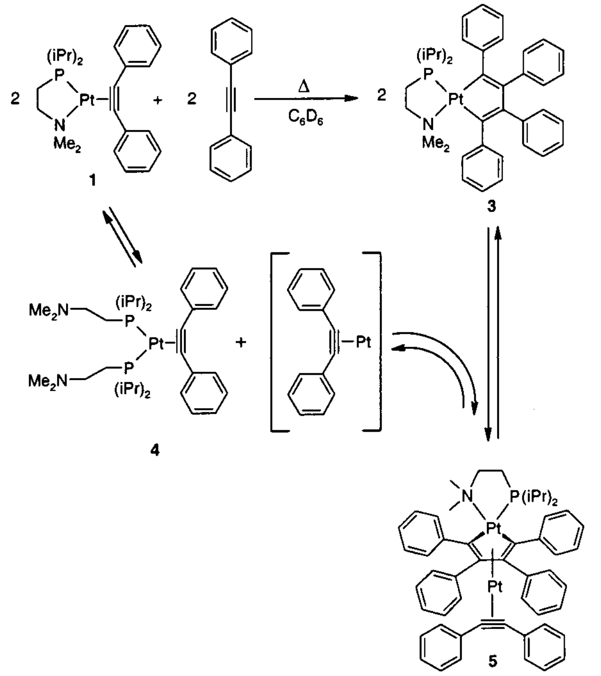
Scheme 2



1

3

Scheme 3



1

3

4

5

ylacetylene at all. However, an equilibrium between **1** and compound **4**, which contains two P,N ligands, must also exist according to the data obtained by $^{31}P\{^1H\}$ NMR spectroscopy (Figure 4). The remaining fragment "Pt(η^2-PhC≡CPh)" would react very fast with the metallacycle **3** to form the second intermediate **5** (Scheme 3). This is consistent with the observation that the relative amounts of **4** and **5** remain almost equal during the course of the reaction. The highest concentrations of **4** and **5** were detected after 2.5 h of thermolysis. The latter reaction is also reversible, leading again to a decrease of **5** as well as **4** to form the final product **3** quantitatively after approximately 68.5 h at $T = 78$ °C. A distribution of species plot is shown in Figure 6. The amount of the starting material **1** decreases rapidly at the beginning of the reaction. The intermediates **4** and **5** are formed early in the reaction, whereas the metallacycle **3** is formed comparatively slow. These data are consistent with a complex rapid equilibration of species prior to a slower formation of product.

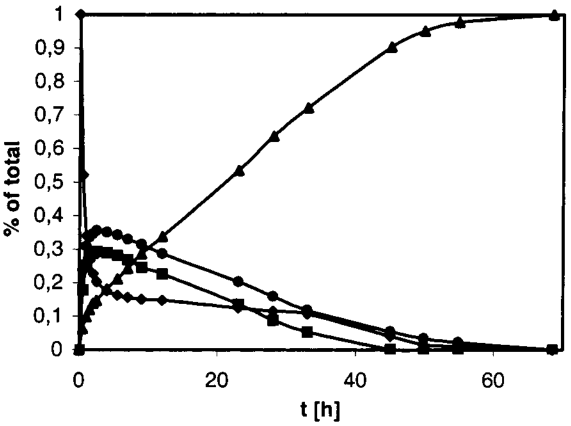


Figure 6. Distribution of species **1**, **3**, **I** (**4**), and **II** (**5**) in the reaction of **1** with diphenylacetylene ($T = 78$ °C) (◆, **1**; ▲, **3**; ■, **4**; ●, **5**).

Conclusions

The Pt(0) complex (PN)Pt(η^2-PhC≡CPh) reacts with diphenylacetylene to form quantitatively the metalacyclic product (PN)Pt(CPh)$_4$. Two transient intermediates are observed during the course of the reaction and were independently synthesized and characterized. Intermediate **I** turned out to be a Pt(η^2-PhC≡CPh) complex with two P,N ligands attached to the metal center via the phosphorus donor. In intermediate **II** a Pt(η^2-PhC≡CPh) fragment is η^4-coordinated to the double-bond system of the final product, the metalacycle (PN)Pt(CPh)$_4$. In contrast, no reaction at all is observed in the corresponding bisphosphino-substituted complex (dippe)Pt(η^2-PhC≡CPh). These studies demonstrate that the P,N ligand is labile not only at the nitrogen but at the phosphorus atom also. This enhanced lability, compared to the dippe analogue, results in far more varied reactivity as summarized in this report. Ultimately thermodynamics takes over and a single simple metalacycle product is formed.

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation glovebox unless otherwise stated. The solvents were commercially available and distilled from dark purple solutions of benzophenone ketyl. A Siemens-SMART three-circle CCD diffractometer was used for the X-ray crystal structure determinations. The elemental analyses were obtained from Desert Analytics. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AMX-400 or Bruker Avance-400 spectrometer, and all ^1H chemical shifts are reported relative to the residual proton resonance in the deuterated solvents. (PN)Pt(η^2-PhC≡CPh),[9] (dippe)Pt(η^2-PhC≡CPh),[9] (COD)Pt(PhC≡CPh),[7b] Pt(PhC≡CPh)$_2$,[7a,b] (^{i}Pr)$_2$PCH$_2$CH$_2$NMe$_2$ (PN),[11] and (^{i}Pr)$_2$PCH$_2$CH$_2$P(^{i}Pr)$_2$ (dippe)[12] were synthesized according to published procedures.

Preparation of (PN)Pt(CPh)$_4$ (3). (Diisopropylphosphinodimethylamino)ethane) (6.7 μL, 0.032 mmol) was added dropwise to a solution of Pt(η^2-PhC≡CPh)$_2$ in C$_6$D$_6$ (0.5 mL). A bright yellow solution was formed and was transferred to an NMR tube. The ^{31}P NMR spectrum was recorded immediately and showed the quantitative formation of **1** and 1 equiv of diphenylacetylene. The solution was then heated to $T = 100$ °C and the starting material was quantitatively converted to **3** within 42 h. The solvent was removed in vacuo, and the remaining solid was recrystallized from pentane/CH_2Cl_2 (6:1) at $T = -30$ °C. **3** was obtained as a colorless solid. Yield: 15.6 mg (0.021 mmol, 66%). ^{1}H NMR (C_6D_6): δ (ppm) 0.62 (dd, $^3J_{H-P} = 10.7$ Hz, $^3J_{H-H} = 6.9$ Hz, 6 H, ^{i}Pr), 0.76 (m, 2 H, $-CH-$), 1.07 (m, 2 H, $P-CH_2-$), 1.16 (m, 6 H, ^{i}Pr), 1.63 (m, 2 H, $N-CH_2-$), 2.02 (s, br, 6 H, $N-CH_3$), 6.67 (t, 2 H, m-C_6H_5), 6.85−6.97 (m, 6 H, 2×m-C_6H_5, 4×p-C_6H_5), 6.96 (t, 2 H, m-C_6H_5), 7.08 (t, 2 H, m-C_6H_5), 7.24 (d, $^3J_{H-H} = 8.0$ Hz, 2 H, o-C_6H_5), 7.28 (d, $^3J_{H-H} = 7.4$ Hz, 2 H, o-C_6H_5), 7.33 (d, $^3J_{H-H} = 7.0$ Hz, 2 H, o-C_6H_5), 7.44 (d, $^3J_{H-H} = 7.5$ Hz, 2 H, o-C_6H_5). ^{13}C{^{1}H} NMR (C_6D_6): δ (ppm) 16.2 (d, $^2J_{C-P} = 18.9$ Hz, $-CH-CH_3$), 17.9 (d, $^2J_{C-P} = 6.4$ Hz, $-CH-CH_3$), 22.4, 22.5, 22.6, 22.7 ($P-CH_2-$; $-CH-$), 49.3 ($N-CH_3$), 67.5 (d, $^2J_{C-P} = 7.4$ Hz, $N-CH_2-$), 123.4, 123.8, 124.2, 126.8, 127.3, 127.5, 128.5, 129.3 (Ph−C), 130.0 (d, $J = 2.3$ Hz, Ph−C), 131.0 (Ph−C), 139.6, 143.8 (d, $J = 6.5$ Hz), 152.6 (d, $J = 4.9$ Hz), 154.3 (d, $J = 4.7$ Hz), 155.9 (d, $J = 4.7$ Hz), 157.2, 166.5, 167.6 (vinylic-C, ipso-Ph-C). ^{31}P NMR (C_6D_6): δ (ppm) 52.8 (s, with platinum satellites, $^1J_{Pt-P} = 2228$ Hz). Anal. Calcd for $C_{38}H_{44}NPPt$ (740.82 g/mol): C, 61.61; H, 5.99; N, 1.89. Found: C, 61.83; H, 6.22; N, 1.96.

Preparation of $(NP)_2Pt(\eta^2\text{-}PhC{\equiv}CPh)$ (4). A solution of $(^iPr)_2PCH_2CH_2NMe_2$ (11.3 μl, 0.054 mmol) in CD_2Cl_2 (0.5 mL)-was cooled to $T = -30$ °C and added to a precooled vial containing (COD)Pt(PhC≡CPh) (12.4 mg, 0.026 mmol). A yellow solution was formed, and the reaction was monitored by ^{31}P NMR spectroscopy. **4** was quantitatively generated within 8 h. The solvent and all volatile compounds were removed in vacuo. **4** was isolated as a yellow, air- and moisture-sensitive oil. ^{1}H NMR (C_6D_6): δ (ppm) 1.05 (dd, $^3J_{H-P} = 12.8$ Hz, $^3J_{H-H} = 6.9$ Hz, 6 H, ^{i}Pr, m, 4 H, $-CH-$), 1.20 (dd, $^3J_{H-P} = 15.1$ Hz, $^3J_{H-H} = 7.2$ Hz, 6 H, ^{i}Pr), 2.07 (m, 4 H, $P-CH_2-$), 2.12 (s, br, 12 H, $N-CH_3$), 2.52 (m, br, 4 H, $N-CH_2-$), 7.00 (t, $^3J_{H-H} = 6.6$ Hz, 2 H, p-C_6H_5), 7.19 (t, 4 H, m-C_6H_5), 7.53 (d, $^3J_{H-H} = 7.1$ Hz, 4 H, o-C_6H_5). ^{13}C{^{1}H} NMR (C_6D_6): δ (ppm) 18.9 (s, with platinum satellites, $^3J_{C-Pt} = 19.7$ Hz, $-CH-CH_3$), 20.2 (m, $-CH-CH_3$), 25.2 (m, $P-CH_2-$), 27.2 (m, $-CH-$), 45.2 ($N-CH_3$), 56.1 (s, with platinum satellites, $^3J_{C-Pt} = 22.0$ Hz, $N-CH_2-$), 125.0, 128.6, 131.9 (Ph−C), 140.4 (m, $\equiv C-Ph$). ^{31}P NMR (C_6D_6): δ (ppm) 32.3 (s, with platinum satellites, $^1J_{Pt-P} = 3336$ Hz). Anal. Calcd for $C_{34}H_{58}N_2P_2Pt$ (751.93 g/mol): C, 54.31; H, 7.77; N, 3.73. Found: C, 53.60; H, 7.83; N, 3.48.

Preparation of $(PN)Pt(CPh)_4Pt(\eta^2\text{-}PhC{\equiv}CPh)$ (5). Pt(η^2-PhC≡CPh)$_2$ (13.0 mg, 0.024 mmol) was dissolved in C_6D_6 (0.5 mL). $(^iPr)_2PCH_2CH_2NMe_2$ (5.0 μl, 0.024 mmol) was added, and an orange solution was formed. This solution was transferred to a vial containing more Pt(PhC≡CPh)$_2$ (13.0 mg, 0.024 mmol). The orange solution, which slowly turned dark orange, was transferred to an NMR tube and heated to $T = 70$ °C. The reaction was monitored by ^{31}P NMR spectroscopy. During the course of the reaction the color changed to dark red and a dark red solid was formed. **5** was formed in ~95% spectroscopic yield within 21 h. The volume was reduced in vacuo to ~0.1 mL, and 2 mL of petroleum ether was added. The red solid was filtered, washed with petroleum ether, and dried in vacuo. Yield: 18.0 mg (0.016 mmol, 68%). ^{1}H NMR (THF-d_8): δ (ppm) 0.80 (m, 2 H, $-CH-$), 0.89 (m, 3 H, ^{i}Pr), 0.99 (dd, $^3J_{H-P} = 10.6$ Hz, $^3J_{H-H} = 6.8$ Hz, 3 H, ^{i}Pr), 1.22 (dd, $^3J_{H-P} = 18.1$ Hz, $^3J_{H-H} = 6.9$ Hz, 3 H, ^{i}Pr), 1.37 (dd, $^3J_{H-P} = 17.9$ Hz, $^3J_{H-H} = 7.9$ Hz, 3 H, ^{i}Pr), 1.50 (m, 2 H, $P-CH_2-$), 1.93 (s, br, 3 H, $N-CH_3$), 2.30 (m, 2 H, $N-CH_2-$), 2.38 (s, br, 3 H, $N-CH_3$), 6.61−6.85 (m, 12 H, phenyl−H), 7.20 (pt, 4 H, phenyl−H), 7.31 (pt, 7 H, phenyl−H), 7.38 (d, $^3J_{H-H} = 7.2$ Hz, 2 H, o-C_6H_5), 7.72 (d, $^3J_{H-H} = 6.8$ Hz, 1 H, o-C_6H_5), 7.80 (d, $^3J_{H-H} = 7.4$ Hz, 4 H, o-C_6H_5). ^{31}P NMR (THF-d_8): δ (ppm) 49.9 (s, with platinum satellites, $^1J_{Pt-P} = 2661$ Hz). Anal. Calcd for $C_{52}H_{54}NPPt_2$ (1114.17 g/mol): C, 56.06; H, 4.89; N, 1.26. Found: C, 56.43; H, 4.81; N, 1.12.

Thermolysis of 1. An equimolar solution of **1** and diphenylacetylene was prepared by adding $(^iPr)_2PCH_2CH_2NMe_2$ (6.4 μL, 0.03 mmol) to a solution of Pt(PhC≡CPh)$_2$ (16.8 mg, 0.03 mmol) in C_6D_6 (0.5 mL). The orange solution was transferred to a resealable NMR tube and heated to $T = 78$ °C. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. **3** was quantitatively formed after 68.5 h.

Thermolysis of 2. Diphenylacetylene (3.2 mg, 0.018 mmol) was added to a solution of **2** (10.9 mg, 0.017 mmol) in C_6D_6 (0.5 mol). The orange solution was transferred to a resealable NMR tube and heated to $T = 100$ °C. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. No reaction was observed within 6 days.

Catalytic Formation of Hexaphenylbenzene. $(^iPr)_2PCH_2CH_2NMe_2$ (5.8 μL, 0.027 mmol) was added to a solution of Pt(PhC≡CPh)$_2$ (15.1 mg, 0.027 mmol) in C_6D_6 (0.5 mL). Diphenylacetylene (53.7 mg, 0.3 mmol) was added, and the orange solution was transferred to a sealable NMR tube and heated to $T = 100$ °C. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. A total of 40 mg (74%) hexaphenylbenzene was isolated after 150 days of thermolysis.

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Supporting Information Available: Details of data collection parameters, bond lengths, bond angles, fractional atomic coordinates, and anisotropic thermal parameters for **1**, **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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