Phosphaazaallene Dimerization and Phosphaallene Isomerization: Catalysis by Zerovalent Palladium and Platinum Complexes

Marie-Anne David, John B. Alexander, and David S. Glueck*

6128 Burke Laboratory, Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Glenn P. A. Yap, Louise M. Liable-Sands, and Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received September 12, 1996[⊗]

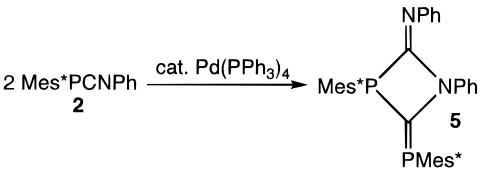
Several Pd(0) complexes catalyze the dimerization of Mes*PCNPh [**2**, Mes* = 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$] to the unsymmetrical heterocycle Mes*P(μ-CNPh)NPh(μ-CPMes*) (**5**). The symmetrical dimer [Mes*P(μ-CNPh)]$_2$ (**7**), which forms slowly by uncatalyzed dimerization of **2**, does not interconvert with **5**; both **5** and **7** were structurally characterized by X-ray crystallography. The Pt complexes PtL$_2$[η^2-(*P*,*C*)-Mes*PCNPh] [**8**, L = $^1/_2$ dppe (Ph$_2$PCH$_2$-CH$_2$PPh$_2$); **9**, L = PPh$_3$; **10**, L = PCy$_3$ (Cy = c-C$_6$H$_{11}$)], models for intermediates in the catalysis, were prepared. Isomerization of Mes*PCCPh$_2$ (**3**) to the phosphaindan [2,4-(*t*-Bu)$_2$C$_6$H$_2$(6-CMe$_2$CH$_2$PCH=CPh$_2$)] (**6**), which we previously observed with Rh(I) catalysts, is catalyzed by Pt(PCy$_3$)$_2$ or the known Pt(PPh$_3$)$_2$[η^2-(*P*,*C*)-Mes*PCCPh$_2$] (**12**). Comparison of the metal-mediated reactions of **2** and **3** suggests that the initial steps in the catalyses, coordination of the phosphacumulene to M(0), followed by loss of a ligand, are similar.

Introduction

The steric protection afforded by the bulky supermesityl group [Mes* = 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$] has recently allowed the synthesis of a series of stable phosphacumulenes, including the phosphaketene[1] Mes*PCO (**1**), the phosphaazaallene Mes*PCNPh (**2**), the phosphaallene Mes*PCCPh$_2$ (**3**),[2] and the diphosphaallene Mes*-PCPMes* (**4**).[3] Although these molecules are highly reactive and could conceivably bind to transition metals in a variety of ways, their coordination chemistry and metal-mediated transformations are relatively unexplored.[4]

We report here a new mode of reactivity for phosphaazaallene **2**, its dimerization to the unsymmetrical heterocycle Mes*P(μ-CNPh)NPh(μ-CPMes*) (**5**), catalyzed by Pd(0) complexes. The mechanism of this reaction was investigated by the preparation of related Pt(0) complexes of **2**. Similar zerovalent Pt complexes catalyze isomerization of **3** to the phosphaindan [2,4-(*t*-Bu)$_2$C$_6$H$_2$(6-CMe$_2$CH$_2$PCH=CPh$_2$)] (**6**), which we previously observed with isoelectronic Rh(I) catalysts.[4h]

Scheme 1



Results

Phosphaazaallene Dimerization. Pd(PPh$_3$)$_4$ catalyzes dimerization of **2** to Mes*P(μ-CNPh)NPh(μ-CPMes*) (**5**) in 98% yield as spectroscopically pure brown-orange crystals (Scheme 1). The reaction proceeds quickly in THF at room temperature. After several recrystallizations from petroleum ether dimer **5** is obtained as pale yellow analytically pure crystals. Formation of **5** is also catalyzed by Pd(dba)$_2$ (dba = dibenzylideneacetone) (at room temperature) and by Pd(dppe)$_2$ [dppe = 1,2-bis-(diphenylphosphino)ethane] (slowly at 60 °C).

Dimer **5** was characterized by multinuclear NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum shows peaks at δ 111 (d, $^2J_{P-P}$ = 124 Hz, C=PMes*) and 32 (d, $^2J_{P-P}$ = 124 Hz, Mes*P) due to the two different phosphorus

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.

(1) Appel, R.; Paulen, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 785−786.

(2) For synthesis of **2** and **3**, see: Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 1809−1812. For structural and theoretical studies of these compounds, see: (a) Yoshifuji, M.; Niitsu, T.; Toyota, K.; Inamoto, N.; Hirotsu, K.; Odagaki, Y.; Higuchi, T.; Nagase, S. *Polyhedron* **1988**, *7*, 2213−2216. (b) Yoshifuji, M.; Toyota, K.; Inamoto, N.; Hirotsu, K.; Higuchi, T.; Nagase, S. *Phosphorus Sulfur* **1985**, *25*, 237−243. (c) Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1999−2004. (d) Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1985**, 2005−2012.

(3) (a) Yoshifuji, M.; Toyota, K.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1984**, 689−690. (b) Karsch, H. H.; Reisacher, H.-U.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 618−619.

(4) For a review, see: Nixon, J. F. *Chem. Rev.* **1988**, *88*, 1327−1362. See also: (a) Akpan, C. A. D. Phil. Thesis, Sussex, 1986. (b) Akpan, C. A.; Meidine, M. F.; Nixon, J. F.; Yoshifuji, M.; Toyota, K.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1985**, 946−947. (c) Akpan, C. A.; Hitchcock, P. B.; Nixon, J. F.; Yoshifuji, M.; Niitsu, T.; Inamoto, N. *J. Organomet. Chem.* **1988**, *338*, C35−C37. (d) Yoshifuji, M.; Toyota, K.; Sato, T.; Inamoto, N.; Hirotsu, K. *Heteroatom Chem.* **1990**, *1*, 339−342. (e) Yoshifuji, M.; Toyota, K.; Niitsu, T.; Inamoto, N.; Hirotsu, K. *J. Organomet. Chem.* **1990**, *389*, C12−C15. (f) Champion, D. H.; Cowley, A. H. *Polyhedron* **1985**, *4*, 1791−1792. (g) Cowley, A. H.; Pellerin, B.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 6734−6735. (h) David, M.-A.; Paisner, S. N.; Glueck, D. S. *Organometallics* **1995**, *14*, 17−19. (i) David, M.-A.; Glueck, D. S.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 4040−4042. (j) Alexander, J. B.; Glueck, D. S.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 3603−3606.

S0276-7333(96)00782-0 CCC: $14.00

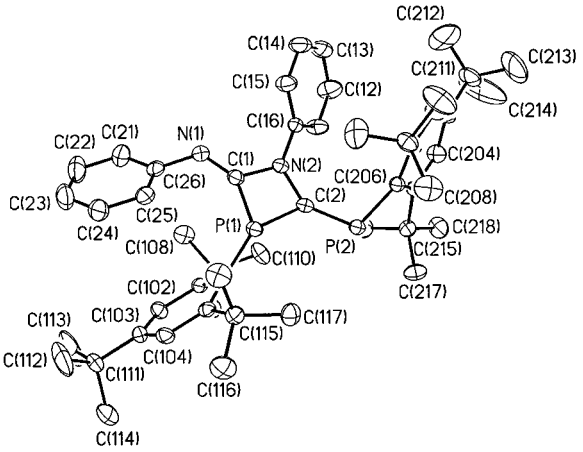


Figure 1. ORTEP diagram of **5.** Selected bond lengths (Å): P(1)−C(1) 1.837(4), P(1)−C(2) 1.857(3), P(2)−C(2) 1.672(4), N(1)−C(1) 1.278(4), N(2)−C(1) 1.405(4), N(2)−C(2) 1.419(4). Selected bond angles (deg): C(1)−P(1)−C(2) 73.2(2), C(1)−N(2)−C(2) 102.5(3), N(1)−C(1)−N(2) 125.3-(3), N(1)−C(1)−P(1) 142.4(3), N(2)−C(1)−P(1) 91.8(2), N(2)−C(2)−P(2) 143.6(2), N(2)−C(2)−P(1) 90.6(2), P(2)−C(2)−P(1) 123.9(2).

nuclei. Signals corresponding to the unsaturated carbons appear in the $^{13}C\{^1H\}$ NMR spectrum at δ 173.3 (dd, $^1J_{P-C} = 96$ Hz, $^3J_{P-C} = 14$ Hz) and at δ 164.3 (dd, $^1J_{P-C} = 28$ Hz, $^3J_{P-C} = 17$ Hz). The IR spectrum shows a band at 1585 cm^{-1} which can be assigned to the C═N stretch.[5]

The ^1H NMR spectrum shows that rotation about the P−C(Mes*) bonds is restricted on the NMR time scale at room temperature. In CD_2Cl_2 at 20 °C four different resonances due to the *ortho t*-Bu groups are observed at δ 1.84, 1.51, 1.48, and 1.32, while the *para t*-Bu groups appear as one peak at δ 1.29 and the *meta* Mes* protons as broad signals at δ 7.46 and 7.24. At −40 °C, the *meta* protons give rise to four peaks (δ 7.46, 7.44, 7.23 and 7.22), and the *para t*-Bu groups show two peaks (δ 1.24 and 1.19). Similarly, the ^{13}C NMR spectrum at room temperature shows 12 different resonances for the Mes* ring carbons.

The structure of **5** was confirmed by X-ray crystallography (Figure 1). Crystal, data collection, and refinement parameters are given in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are given in the Supporting Information. Selected bond lengths and angles appear in the figure caption; full listings are available in the Supporting Information.

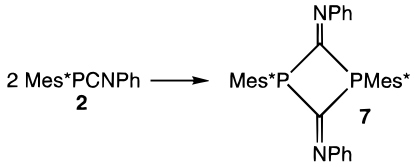
The structure is similar to that of the dimer of the unknown phosphathioketene Mes*PCS.[6] The four-membered ring is bent with an angle of 165.5° between the C(1)−P(1)−C(2) and C(1)−N(2)−C(2) planes. It is more distorted [angles at P(1) and N(2): 73.2(2) and 102.5(3)°] than the phosphathioketene dimer [angles at P and S: 84 and 86°]. The P−C bond lengths in the ring [1.837(4) and 1.857(3) Å] are longer than those in the thio analog [1.806(9) and 1.805(8) Å], but the exocyclic P═C bond lengths are very similar in the two compounds [1.672(4) and 1.673(8) Å, respectively]. The N═C bond length [1.278(4) Å] is comparable to those reported previously.[7]

Table 1. Crystallographic Data for 5 and 7

	5	**7**
	(a) Crystal Parameters	
formula	$C_{50}H_{68}N_2P_2$	$C_{50}H_{68}N_2P_2$
fw	759.0	759.0
cryst system	monoclinic	triclinic
space group	*I*2/*a*	$P\bar{1}$
a, Å	28.438(9)	9.942(5)
b, Å	10.589(4)	10.841(6)
c, Å	31.62(1)	11.074(8)
α, deg		85.42(5)
β, deg	101.48(5)	87.81(5)
γ, deg		83.09(4)
V, Å^3	9332(6)	1181(1)
Z	8	1
cryst dimens, mm	0.20 × 0.30 × 0.40	0.40 × 0.42 × 0.43
cryst color	yellow	yellow
D(calc), g cm^{-3}	1.080	1.068
μ(Mo Kα), cm^{-1}	1.27	1.25
temp, K	298	296
	(b) Data Collection	
diffractometer	Siemens P4	
monochromator	graphite	
radiation	Mo Kα (*λ* = 0.710 73 Å)	
2*θ* scan range, deg	4.0−48.0	4.0−50.0
data collcd (*h*,*k*,*l*)	±32,+12,+36	±11,±12,+13
rflns, collcd	7461	4385
indpt. rflns	7307	4148
indpt obsvd rflns $F_o \geq 4\sigma(F_o)$	3554	3170
	(c) Refinement[a]	
R(*F*), %	5.27[b]	5.31[a]
R(w*F*), %	11.86[b,c]	7.93[a]
Δ/*σ*(max)	0.00	0.02
Δ(*ρ*), e Å^{-3}	0.39	0.34
N_o/N_v	15.0	11.6
GOF	1.09	1.43

[a] Quantity minimized = $\sum w\Delta^2$; $R = \sum\Delta/\sum(F_o)$; $R(w) = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$. [b] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. [c] $R(wF^2)$, %.

Scheme 2



In the absence of the Pd(0) complexes, **2** undergoes a slower dimerization on standing in solution or in the solid state. In this case, the symmetrical product [Mes*P(*μ*-CNPh)]$_2$ (**7**) is formed (Scheme 2). Related heterocycles have been previously obtained as a mixture of *E*- and *Z*-isomers,[8] and their formation has been attributed to [2+2]-cycloaddition at the P═C bond of the corresponding unobserved phosphacumulenes. Dimer **7** exists in solution as one isomer, presumably the *E* one as observed in the solid state (see below). The $^{31}P-\{^1H\}$ NMR spectrum shows one peak at 10 ppm and the $^{13}C\{^1H\}$ NMR spectrum a triplet ($^1J_{P-C} = 30$ Hz, CNPh)

(5) (a) Wentrup, C.; Briehl, H.; Becker, G.; Uhl, G.; Wessely, H.-J.; Maquestiau, A.; Flammang, R. *J. Am. Chem. Soc.* **1983**, *105*, 7194−5. (b) Becker, G.; Riffel, H.; Uhl, W.; Wessely, H.-J. *Z. Anorg. Allg. Chem.* **1986**, *534*, 31−49. (c) Becker, G.; Harer, J.; Uhl, G.; Wessely, H.-J. *Z. Anorg. Allg. Chem.* **1985**, *520*, 120−138. (d) Weber, L.; Buchwald, S.; Lentz, D.; Stamm, O.; Preugschat, D.; Marschall, R. *Organometallics* **1994**, *13*, 4406−12. (e) Weber, L.; Dobbert, E.; Buchwald, S.; Stammler, H.-G.; Neumann, B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1407−1413.

(6) (a) Folling, P. Ph.D. Thesis, Bonn, 1988. (b) Appel, R.; Folling, P.; Krieger, L.; Siray, M.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 970−971.

(7) See ref 5d and references cited therein.

(8) See ref 5 and: Appel, R.; Laubach, B. *Tetrahedron Lett.* **1980**, *21*, 2497−2500.

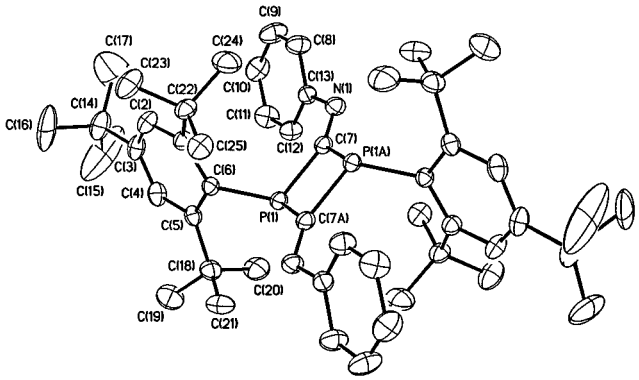


Figure 2. ORTEP diagram of **7**. Selected bond lengths (Å): P(1)−C(6) 1.832(3), P(1)−C(7) 1.833(3), P(1)−C(7A) 1.825(3), P(1)−P(1A) 2.694(2), N(1)−C(7) 1.274(3), N(1)−C(13) 1.416(4). Selected bond angles (deg): C(6)−P(1)−C(7) 117.4(1), C(6)−P(1)−P(1A) 134.9(1), C(7)−P(1)−P(1A) 42.4(1), C(6)−P(1)−C(7A) 125.4(1), C(7)−P(1)−C(7A) 85.1-(1), P(1A)−P(1)−C(7A) 42.7(1), P(1)−C(7)−P(1A) 94.9(1).

at δ 181.9. The IR spectrum exhibits bands at 1543 and 1585 cm^{-1} (ν_{CN}), which are comparable to those reported for related dimers.[5]

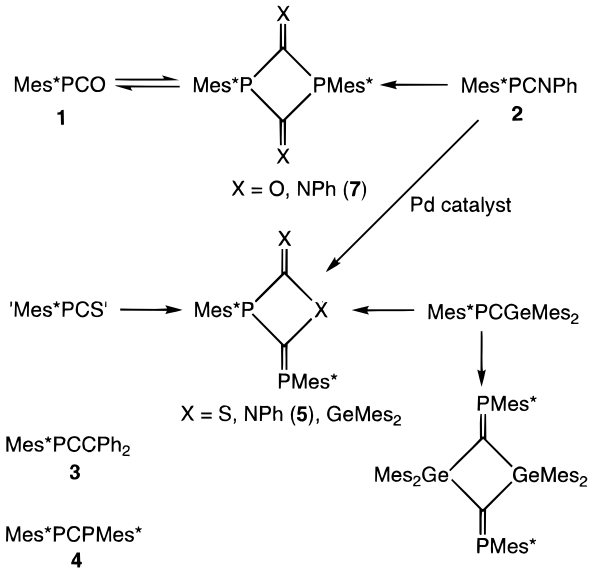
As observed for **5**, rotation about the P−C(Mes*) bonds is restricted on the NMR time scale at ambient temperature. The ^1H NMR spectrum (CD_2Cl_2) shows two different peaks at δ 1.60 (broad) and δ 1.29 (sharp) in a 2:1 ratio, due to the *ortho* and *para* *t*-Bu groups, respectively, while the *meta* protons of the Mes* ring give rise to a broad signal at δ 7.34. At −40 °C, two different peaks due to the *ortho* *t*-Bu groups are resolved at δ 1.64 and 1.51 and the *meta* protons show two different signals at δ 7.35 and 7.26. The ^{13}C NMR spectrum shows six different resonances due to the Mes* ring carbons.

The X-ray crystal structure of **7** is shown in Figure 2, with selected bond lengths and angles in the caption. Crystal, data collection, and refinement parameters are given in Table 1, and atomic coordinates, equivalent isotropic displacement coefficients, and full listings of bond lengths and angles appear in the Supporting Information.

The structure features a planar P_2C_2 ring with trans Mes* substituents. The nitrogen atoms lie in the same plane, and the ipso carbons are 0.187 Å out of the plane. The steric constraints imposed by the Mes* groups require them to be trans to each other and the phenyl substituents to adopt the *E*-configuration. The four-membered ring has a rhombic geometry with the P−C bond lengths [1.833(3) and 1.825(3) Å] and the CPC and the PCP bond angles [85.1(1) and 94.9(1)°, respectively] similar to those in the phosphaketene dimer [Mes*P-(μ-CO)]$_2$.[6a] This compound forms both orthorhombic and monoclinic crystals, in which the ring P−C bond lengths range from 1.838(16) to 1.796(5) Å, with CPC bond angles of 84.1(7) and 81.7(3)° and PCP angles ranging from 98.3(3) to 94.9(8)°. Several heterocycles [RP(μ-CNR′)]$_2$ analogous to **7** but with other, usually sterically less demanding substituents, have been prepared and crystallographically characterized, and their structures are similar to that of **7**.[5b,d]

Under the mild reaction conditions required for the formation of **5** and **7**, the dimerizations are irreversible, and the dimers do not interconvert. On heating to 80 °C in toluene, dimer **5** re-forms a small amount of monomer **2** in addition to other unidentified products. Dimer **7** is stable under these conditions, but irradiation of this compound in toluene gives a small amount of **2**, plus other products (see the Experimental Section).

Chart 1



It is unusual that the phosphaazaallene **2** exists in three different forms, as monomer **2** stabilized by the bulky Mes* group and as the two dimers **5** and **7**, which are themselves sterically hindered but form readily from **2**. In contrast to these observations, Mes*PCO forms only the symmetrical dimer (reversibly), and Mes*PCS exists only as the unsymmetrical dimer.[6] Recently, the phosphagermaallene Mes*PCGeMes$_2$ [Mes = 2,4,6-$Me_3C_6H_2$] was observed at low temperature in solution and found to dimerize on warming to a mixture of products, a symmetrical dimer with two exocyclic C=P bonds and an unsymmetrical one with an exocyclic C=P and a Ge=C bond.[9] Chart 1 shows the reported structures formed by phosphacumulene dimerization and emphasizes the striking effect of the X group on the chemistry of the phosphacumulenes Mes*PCX (note that dimerization of the mono- and diphosphaallenes **3** and **4** has not been observed).

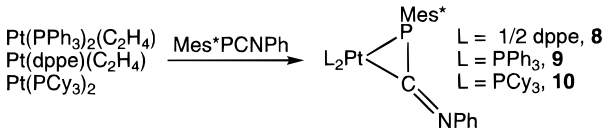
A theoretical study[10] found that dimerization of the parent phosphaketene HPCO to the symmetrical dione product (analogous to **7**) is thermoneutral or slightly exothermic, while formation of the unsymmetrical dimer (analogous to **5**) is endothermic. This is consistent with the experimental observations on dimerization of Mes*PCO. Related calculations suggest that the symmetrical phosphagermaallene dimer [$H_2Ge(\mu$-CPH)]$_2$ is more stable than the unsymmetrical $H_2Ge(\mu$-CPH)PH-(μ-$CGeH_2$); this, however, contradicts the experimental results on the system with bulky Mes* and Mes substituents.[9] In this work, we have not been able to assess relative stabilities of the two phosphaazaallene dimers because of the irreversibility of the dimerizations. However, the kinetically stabilized monomer is thermodynamically less stable than the dimers.

Related platinum chemistry provides information on the mechanism of the Pd-catalyzed dimerization of **2**.

(9) Ramdane, H.; Ranaivonjatovo, H.; Escudie, J.; Mathieu, S.; Knouzi, N. *Organometallics* **1996**, *15*, 3070−3075.

(10) Salzner, U.; Bachrach, S. M. *J. Am. Chem. Soc.* **1994**, *116*, 6850−6855.

Scheme 3



Reactions of "PtL_2" sources with **2** give the adducts PtL_2-[η^2-(P,C)-Mes*PCNPh)] [Scheme 3, L = $^1/_2$ dppe (**8**), PPh_3 (**9**), PCy_3 (**10**, Cy = c-C_6H_{11})]. The orange dppe complex **8** is isolable and was characterized spectroscopically and by elemental analysis. The complexed phosphacumulene in this compound gives rise to an IR band at 1577 cm^{-1} (ν_{CN}, KBr) and a broad peak in the ^{13}C NMR spectrum at 196 ppm (*C*NPh). The PPh_3 and PCy_3 complexes **9** and **10** are unstable in solution and were characterized, by comparison to **8**, by variable-temperature ^{31}P NMR spectroscopy (see below).

The ^{31}P NMR spectra of the phosphaazaallene complexes were investigated over a wide temperature range, and the results, with data for related Pt complexes of phosphacumulenes **3** and **4** for comparison, are summarized in Table 2. These results are consistent with coordination of **2** in the plane of the PtL_2 fragment by the P═C bond, which makes the tertiary phosphine ligands inequivalent and gives rise to different cis and trans **2**-PR_3 couplings. The small $^2J_{P-P}$ and $^1J_{P-Pt}$ couplings to coordinated **2** are characteristic of Pt−phosphacumulene complexes. The central phosphacumulene carbon has a larger trans influence (reflected in $^1J_{Pt-P}$ of the trans ligand) than the cumulene phosphorus, the reverse of the trend observed previously for complexes of the mono- and diphosphaallenes **3** and **4**.

For PCy_3 complex **10**, the expected three P−P couplings, with Pt satellites for the PCy_3 resonances, are readily observed at 22 °C. However, the peak due to complexed Mes*PCNPh was not well resolved, and its Pt satellites were not observed. Higher (up to 62 °C) or lower (down to −60 °C) temperatures did not significantly affect the spectra, improve the peak shapes, or allow observation of these satellites.

At room temperature, the PPh_3 complex is fluxional, as indicated by broad peaks due to complexed PPh_3. At −60 °C in toluene-d_8, the PPh_3 peaks are well-resolved and the data shown in the table can be obtained. At this temperature, the Pt satellites of the complexed phosphaazaallene peak appear as broad lines, and J_{Pt-P} ∼ 200 Hz. At higher temperatures, these signals are better resolved. At 22 °C, for example, an overlapping doublet of doublets (both J_{PP} values ∼26 Hz)[11] with Pt satellites (J_{Pt-P} = 154 Hz) is observed, while the PPh_3 peaks remain broad. The different P−P couplings observed in the complexed cumulene ligand at different temperatures are puzzling, since one might expect that dynamic averaging of the low-temperature structure would give an average coupling constant (43 instead of the observed 26 Hz). Since several different fluxional processes, including restricted rotation about the Pt−cumulene axis, as previously described[4a,b] for related complexes of phosphaallenes **3** and **4**, restricted rotation about the P−C(Mes*) bond, and PPh_3 dissociation/association may be operating simultaneously, we did not investigate the nature of the fluxionality further.

(11) At higher temperatures (up to 82 °C), this peak appeared as a triplet, with similar P−P and Pt−P couplings.

At room temperature, the dppe complex shows broad peaks both for the dppe resonances and for the complexed cumulene [in C_6D_6, δ 47.3 ($^1J_{Pt-P}$ ∼ 2500 Hz, dppe); 45.4 (m, $^1J_{Pt-P}$ ∼ 3030 Hz, dppe); −149 (very broad, Pt satellites not observed, Mes*PCNPh]. At 62 °C, the dppe resonances sharpen and the coupling constants listed in the table are observed. At this temperature the cumulene signal remains broad and its Pt satellites were not observed. At low temperature the spectra are again well-resolved and give parameters similar to those observed at high temperature (Table 2). Interestingly, another species can also be observed at low temperature in THF, toluene, or CD_2Cl_2 and identified most clearly by its signal due to complexed cumulene at δ −157 (THF-d_8, −75 °C, broad d, J = 92; neither additional P−P coupling nor Pt satellites were resolved). One of the dppe resonances for this material can also be observed (δ 53.7, dd, J_{PP} = 40, 92 Hz). The similarity of the chemical shifts and coupling constants for this compound suggest it is an isomer of **8**, presumably due to freezing out of two different conformations. We did not, however, investigate the nature of this complex further.

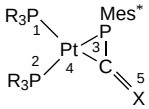
We briefly studied the possible involvement of phosphaazaallene complexes **8**−**10** in catalytic dimerization of **2**. On standing in solution, **9** appears to disproportionate, giving dimer **5**, $Pt(PPh_3)_3$, plus several other unidentified products. Treatment of $Pt(PPh_3)_2(C_2H_4)$ with an excess of **2** gives a mixture containing complex **9**; on heating to 50 °C in THF, catalytic formation of dimer **5** occurs. Complex **10** also decomposes in solution, but in this case no **5** was observed. Addition of excess **2** to **10** at room temperature gives PCy_3 and a mixture of unidentified Pt complexes; this mixture was catalytically inactive in THF at 50 °C. In contrast, dppe complex **8** is stable in solution and does not react with added **2** at room temperature. On heating to 50 °C in THF or C_6D_6, complex **8** decomposes and dimer **5** is formed slowly.

These observations allow speculation about the mechanism of the Pd-catalyzed dimerization of **2** to **5**. A reasonable first step is formation of the adduct PdL_2-[(η^2-(P,C)-Mes*PCNPh], as observed in the Pt complexes. Cumulene coupling could then occur either by direct reaction of **2** with the free N═C bond of the cumulene complex or by phosphine dissociation, complexation of a second 1 equiv of **2**, and dimerization at the metal center. The relative rates of the catalytic reactions mediated by the Pd and Pt PPh_3 complexes, in addition to the slower rates observed for the dppe compounds, suggest that the second of these pathways is operative, although we cannot rule out a possible contribution from the first route. However, the catalytic inactivity of the precursor $Pt(PCy_3)_2$, which binds **2** and then loses PCy_3 readily, as required by the proposed mechanism, shows that the detailed pathway for dimerization remains to be elucidated.

Phosphaallene Isomerization. We previously described isomerization of **3** to the phosphaindan [2,4-(*t*-$Bu)_2C_6H_2$(6-CMe_2CH_2PCH═CPh_2)] (**6**) catalyzed by Rh(I) phosphine complexes (Scheme 4) and the isolation of the catalytically active intermediate [$Rh(PCy_3)$(η^2-(P,C)-Mes*$PCCPh_2$)$Cl]_2$.[4h]

This isomerization is also catalyzed by isoelectronic Pt(0) complexes (Scheme 4). With $Pt(PCy_3)_2$, catalysis

Table 2. Selected ^{31}P NMR Data for Pt Phosphacumulene Complexes[a]

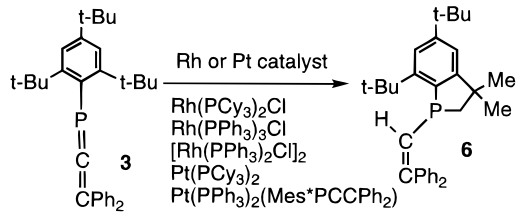


X = NPh; PR_3 = $^1/_2$ dppe (**8**); R = Ph (**9**); R = Cy (**10**)[b]
X = CPh_2; PR_3 = $^1/_2$ dppe (**11**); R = Ph (**12**); R = Et (**13**)[c]
X = PMes*; R = Ph (**14**); R = Et (**15**)[c]

complex	$\delta(P_1)$	$\delta(P_2)$	$\delta(P_3)$	$^2J_{12}$	$^2J_{13}$	$^2J_{23}$	$^1J_{14}$	$^1J_{24}$	$^1J_{34}$
8[d]	49.2 (54.5)	47.0 (50.4)	−146.5 (−144)	48 (45)	14 (12)	88 (101)	2466 (2480)	3055 (3050)	*e* (345)
9[f]	30.8	39.9	−140.2	29	17	69	2794	3342	∼200
10[g]	29.3	37.5	−162.9	22	21	65	2531	3235	e
11	44.7	46.2	−96.3	e	36.6	87.9	2964	2920	234
12[h]	25.4	24.3	−70.6	e	29.3	63.5	3313	3198	192
13	14.7	6.4	−105.1	13.5	21.8	−75.3	3053	2994	268
14[h,i]	21	25.5	237.2	26.3	75.6	72.5	3457	3127	318
15[i]	5.2	13.4	223.2	20.8	44.7	74.4	3269	3070	229

[a] Chemical shifts in ppm (reference 85% H_3PO_4); couplings in Hz. Spectra were obtained at ambient temperature unless specified. [b] This work. [c] Akpan, C. A. D. Phil. Thesis, Sussex, 1986. See also: Akpan, C. A.; Meidine, M. F.; Nixon, J. F.; Yoshifuji, M.; Toyota, K.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1985**, 946−947. [d] Toluene, 62 °C. Values in parentheses in THF-d_8, −75 °C, major isomer (see text). Minor isomer: $\delta_2 = 53.7$, $\delta_3 = -157$, $J_{12} = 40$, $J_{23} = 92$. [e] Not observed. [f] Toluene-d_8, −60 °C. [g] Toluene-d_8. [h] Toluene, −40 °C. [i] Additional data: for **14**, $\delta_5 = -47.2$, $J_{15} = 0$, $J_{25} = 52.8$, $J_{35} = 10.9$, $J_{45} = 239$. For **15**, $\delta_5 = -76.4$, $J_{15} = 5.9$, $J_{25} = 56.6$, $J_{35} = 11.9$, $J_{45} = 213$.

Scheme 4



proceeds slowly in THF at room temperature over several days, and several unidentified intermediates can be observed by ^{31}P NMR. The isolable phosphaallene adduct $Pt(PPh_3)_2(Mes*PCCPh_2)$ (**11**), previously reported[4a] by Akpan, also catalyzes the rearrangement, slowly, on heating to 55 °C in THF. The known[4a] complex $Pt(dppe)(Mes*PCCPh_2)$ (**12**) is, however, not an active catalyst, and no isomerization of **3** is observed on heating a mixture of the phosphaallene and **12** in THF at 55 °C for 3 d.

These observations suggest that the isomerization occurs via the 14-electron monophosphine intermediate $PtL(Mes*PCCPh_2)$, which is isoelectronic to the proposed Rh intermediate $RhL(Cl)(Mes*PCCPh_2)$ we described previously. This mechanism, in its requirement for phosphine dissociation, satisfactorily rationalizes the enhanced activity of the complex containing the bulky PCy_3 in comparison to the PPh_3 derivative and the inert nature of the chelating dppe complex.

Conclusions

We have described new catalyzed and uncatalyzed dimerizations of the kinetically stabilized phosphaazaallene **2** and the use of Pt catalysts for the isomerization of phosphaallene **3**. These studies suggest that the catalytic transformations of these two substrates proceed initially in both cases by formation of a phosphacumulene adduct $ML_2[\eta^2$-(*P*,*C*)-Mes*PCX] (X = NPh or CPh_2), which must lose L before further chemistry can occur. In one case, it appears that another equivalent of phosphaazaallene **2** must bind to the metal to allow rapid dimerization, but isomerization of phosphaallene **3** appears to proceed directly from the intermediate $Pt(L)(Mes*PCCPh_2)$.

Experimental Section

General Methods. For general experimental and spectroscopic procedures, see a recent paper from our group.[12] The following complexes were prepared by the literature methods: Mes*PCNPh,[2] $Mes*PCCPh_2$,[2] $Pd(dba)_2$,[13a] $Pd(PPh_3)_4$,[13b] $Pt(PCy_3)_2$,[14] $Pt(PPh_3)_2(C_2H_4)$,[15] $Pt(dppe)(Mes*PCCPh_2)$,[4a] $Pt(PPh_3)_2(Mes*PCCPh_2)$.[4a] $Pd(dppe)_2$ was prepared by $NaBH_4$ reduction of $Pd(dppe)Cl_2$ in the presence of dppe. $Pt(dppe)(C_2H_4)$ was made using the procedure described for the PPh_3 derivative.

$Pd(PPh_3)_4$-Catalyzed Formation of Mes*P(μ-CNPh)-NPh(μ-CPMes*) (5) from Mes*PCNPh (2). To a solution of Mes*PCNPh (**2**, 152 mg, 0.4 mmol) in THF (1 mL) was added $Pd(PPh_3)_4$ (10 mg, 0.009 mmol). The mixture became brown immediately and was stirred at room temperature for 1 h. The solvent was removed in vacuo, and complex **5** was extracted with petroleum ether (5 mL) from the resulting residue. $Pd(PPh_3)_4$ (10 mg), insoluble in petroleum ether, was recovered from the residue and identified by comparison of its IR and ^{31}P and ^{1}H NMR spectra to the literature values. Cooling of the petroleum ether solution to −25 °C gave **5** as yellow-brown crystals [mp 205 −206 °C (dec), 149 mg, 98% yield].

^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.46 (broad, 2H); 7.24 (broad, 2H); 7.11−7.06 (m, 4H); 6.97−6.84 (m, 6H); 1.84 (broad, 9H, *ortho t*-Bu); 1.51 (9H, *ortho t*-Bu); 1.48 (9H, *ortho t*-Bu); 1.32 (9H, *ortho t*-Bu); 1.29 (18H, *para t*-Bu). ^{1}H NMR (CD_2Cl_2, −40 °C): δ 7.46 (1H); 7.44 (1H); 7.23 (1H); 7.22 (1H); 7.13−7.08 (m, 4H); 6.97−6.84 (m, 6H); 1.79 (9H, *ortho t*-Bu); 1.45 (9H, ortho *t*-Bu); 1.39 (9H, *ortho t*-Bu); 1.28 (9H, *ortho t*-Bu); 1.24 (9H, *para t*-Bu); 1.19 (9H, *para t*-Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 173.3 (dd, $^1J_{P-C}$ = 96 Hz, $^1J_{P-C}$ = 14 Hz, quat CPMes*); 164.3 (dd, $^1J_{P-C}$ = 28 Hz, $^3J_{P-C}$ = 17 Hz, CNPh); 160.7 (broad, quat Ar); 160.2 (broad, quat Ar); 157.3 (broad, quat Ar); 155.2 (broad, quat Ar); 153.7 (broad, quat Ar); 153.1 (broad, quat Ar); 150.2 (Ar); 147.5 (broad, quat Ar); 136.9 (Ar); 133.3 (dd, $^1J_{P-C}$ = 66 Hz, $^3J_{P-C}$ = 9 Hz, quat Ar); 129.0 (Ar); 128.0 (Ar); 127.0 (d, $^1J_{P-C}$ = 67 Hz, quat Ar); 126.3 (Ar); 125.4 (Ar); 124.0 (Ar); 123.3 (broad, Ar); 122.2 (d, $^4J_{P-C}$ = 3 Hz, Ar); 122.0 (Ar); 121.5 (Ar); 39.2−39.1 (broad, quat); 38.5 (broad,

(12) Kourkine, I. V.; Chapman, M. B.; Glueck, D. S.; Eichele, K.; Wasylishen, R. E.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 1478−1485.
(13) (a) Ukai, T.; Kawazawa, H.; Ishii, Y.; Bonnett, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253. (b) Coulson, D. R. *Inorg. Synth.* **1990**, *28*, 107−109.
(14) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850−5858.
(15) Blake, D. M.; Roundhill, D. M. *Inorg. Synth.* **1978**, *18*, 120−125.

quat); 38.4 (quat); 35.2 (quat); 35.1 (quat); 34.9 (broad, quat); 33.7 (*ortho t*-Bu); 33.6 (*ortho t*-Bu); 33.5 (*ortho t*-Bu); 33.4 (*ortho t*-Bu); 31.6 (*para* CH_3); 31.3 (*para* CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 111 (d, $^2J_{P-P} = 124$ Hz); 32 (d, $^2J_{P-P} = 124$ Hz). IR (KBr): 2963, 2901, 2866, 1634, 1585, 1481, 1391, 1358, 1336, 1237 (shoulder), 1218, 1107, 976, 872, 778 (shoulder), 754, 692 cm^{-1}. Anal. Calcd for $C_{50}H_{68}N_2P_2$: C, 79.10; H, 9.05, N, 3.69. Found: C, 78.95; H, 9.43; N, 3.57.

The thermolysis of this compound in toluene was monitored by ^{31}P NMR. After 5 h at 80 °C, some (~10%) decomposition had occurred to give **2** and an unknown compound (−3.4 ppm). Further heating at 90 °C for 6 h caused further decomposition to these products; heating for 3d gave these and several other products, although the starting material was still the major species present. Irradiation of this compound in toluene for 5 h caused partial decomposition to unidentified compounds (^{31}P NMR δ 156 and −3.2 ppm).

Uncatalyzed Formation of [Mes*P(μ-CNPh)]$_2$ (7) from 2. Mes*PCNPh (**2**) dimerizes slowly into **7** on standing in THF or petroleum ether solution at −25 °C or ambient temperature. Small amounts of **7** are formed reproducibly from **2**, but we did not investigate the yield of this reaction or the possible role of trace impurities. Dimer **7** was recrystallized as yellow crystals [mp 227−228 °C (dec)] from a 1:2 mixture of THF/petroleum ether at −25 °C.

^1H NMR (CD_2Cl_2, 20 °C): δ 7.34 (broad, 4H, Ar); 6.93−6.78 (m, 6H, Ar); 6.64−6.62 (m, 4H, Ar); 1.60 (broad, 36H, *ortho t*-Bu); 1.29 (18H, *para t*-Bu). ^1H NMR (CD_2Cl_2, −40 °C): δ 7.35 (d, $^4J_{P-H} = 2$ Hz, 2H); 7.26 (d, $^4J_{P-H} = 2$ Hz, 2H); 6.93−6.78 (m, 6H, Ar); 6.63−6.60 (m, 4H, Ar); 1.64 (18H, *ortho t*-Bu); 1.51 (18H, *ortho t*-Bu); 1.27 (18H, *para t*-Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 182.2 (t, $^1J_{P-C} = 30$ Hz, quat CNPh); 159.8 (broad, quat Ar); 158.1 (broad, quat Ar); 154.0 (quat Ar); 151.9−151.5 (m, quat Ar); 128.7 (Ar); 127.3 (t, $^3J_{P-C} = 31$ Hz, quat Ar); 124.5 (Ar); 124.0 (broad, Ar); 123.0 (broad, Ar); 120.6 (Ar); 39.0 (broad, quat); 35.4 (quat); 34.1 (broad, ortho CH_3); 33.5 (broad, ortho CH_3); 31.3 (para CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 10. IR (KBr): 3455, 2964, 2868, 1627, 1585, 1543, 1483, 1392, 1363, 1238, 1202, 1124, 1070, 1021, 908, 873, 759, 746, 693, 597, 543 cm^{-1}. Anal. Calcd for $C_{50}H_{68}N_2P_2$: C, 79.10; H, 9.05; N, 3.69. Found: C, 78.64; H, 9.24; N, 3.70.

The thermolysis of this compound in toluene was monitored by ^{31}P NMR. After 12 h at 80 °C, no decomposition was observed. Irradiation of this compound for 5 h in toluene caused partial decomposition to **2**, the metalated secondary phosphine [2,4-(*t*-Bu)$_2$C$_6$H$_2$(6-CMe$_2$CH$_2$)PH],[16] and two other unidentified compounds (^{31}P NMR: δ −59.6 and −77.8 ppm).

X-ray Structure Determinations for 5 and 7. Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals for single-crystal X-ray diffraction were selected and mounted within thin, nitrogen-flushed glass capillaries. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° < 2\theta < 25°$).

No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data for **7**. The systematic absences in the diffraction data for **5** were consistent with the monoclinic space groups *Ia* and *I*2/*a*. *E*-statistics suggested the centrosymmetric space group options. The space group choices were subsequently verified by chemically reasonable results of refinement. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix, least-squares procedures. The molecular structure for **7** is located on an inversion center. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in either the SHELXTL (5.3) or the SHELXTL PLUS (4.2) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

Pt(dppe)(Mes*PCNPh) (8). A yellow THF (3 mL) solution of **2** (39 mg, 0.10 mmol) was added to a tan solution of Pt(dppe)(C_2H_4) (64 mg, 0.10 mmol) in THF (3 mL). The resulting orange suspension was then filtered through Celite. The clear orange filtrate was concentrated in vacuo, layered with petroleum ether, and cooled to −20 °C. The resulting white microcrystalline precipitate was removed, and further crystallizations gave **8** as a yellow-orange powder (42 mg, 43%). An analytical sample (orange crystals) was obtained by recrystallization from ether/petroleum ether at −20 °C.

^1H NMR (C_6D_6): δ 7.84 (broad, 4H); 7.53 (4H); 7.20 (broad, 2H); 6.99 (broad, 14H), 6.85 (broad, 3H), 1.79 (broad, 18H), 1.42−1.38 (broad m, 4H), 1.34 (9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 196 (broad, *C*NPh); 156.6 (broad, ortho Mes*); 147.7 (quat Ar); 133.7−133.0 (m, Ar); 130.7 (Ar); 129.0−128.7 (m, Ar); 128.4 (Ar); 123.0 (Ar); 122.2 (Ar); 121.3 (Ar); 38.3 (quat *C*Me$_3$); 34.9 (quat *C*Me$_3$); 33.7 (d, $J = 8.8$, ortho C*Me$_3$*); 31.6 (para C*Me$_3$*); 30.0−29.0 (m, CH_2). IR (KBr): 3050, 2961, 2863, 2362, 2341, 1734, 1700, 1637 (shoulder), 1577, 1540, 1521, 1506, 1480, 1435, 1457, 1435, 1390, 1360, 1098 cm^{-1}. Anal. Calcd for $C_{51}H_{58}NP_3Pt$: C, 62.94; H, 6.02; N, 1.44. Found: C, 62.66; H, 6.28; N, 1.54.

Pt(PR$_3$)$_2$(Mes*PCNPh) (9, R = Ph; 10, R = Cy). These complexes were prepared in toluene or THF from **2** and Pt(PPh$_3$)$_2$(C_2H_4) or Pt(PCy$_3$)$_2$, respectively, and characterized by $^{31}P\{^1H\}$ NMR (Table 2). We were unable to isolate these complexes by recrystallization and observed that they decomposed on standing in solution at room temperature.

Pt-Catalyzed Isomerization of Mes*PCCPh$_2$. Method a. To Pt(PCy$_3$)$_2$ (10 mg, 0.013 mmol) in 1 mL of THF was added Mes*PCCPh$_2$ (30 mg, 0.066 mmol), giving a red solution. After 15 min, the main peak in the ^{31}P NMR spectrum was a broad signal at δ 73.0 (Mes*PCCPh$_2$). The following peaks were also observed: δ 155, 48.8, 34, 11 (PCy$_3$), −23.5 (product isomer **6**), −54.7, −136.5. After 3 d, the solution was orange-yellow, and NMR showed that the major species present was **6**; additional peaks were observed at δ 63 [Pt(PCy$_3$)$_2$], 47.4, 26.6, and −136.6.

Method b. To complex **11** (8 mg, 0.007 mmol) in 1 mL of THF was added an excess of **3** (5 mg, 0.01 mmol), and the orange solution was allowed to stand overnight. No reaction occurred (^{31}P NMR monitoring), so the tube was heated to 55 °C overnight, causing partial isomerization of **6**. Complete conversion required several days. Similar results were observed when **11** was formed in situ by addition of excess phosphaallene **3** to Pt(PPh$_3$)$_2$(C_2H_4).

Acknowledgment. We thank Dartmouth College and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support. We also thank the NSF for a REU fellowship for J.B.A. and Johnson-Matthey/Alfa/Aesar for loans of Pt and Pd salts.

Supporting Information Available: Tables giving details of the X-ray crystal structure determinations for **5** and **7** (14 pages). Ordering information is given on any current masthead page.

OM960782Y

(16) Cowley, A. H.; Pakulski, M. *Tetrahedron Lett.* **1984**, *25*, 2125−2126.