Organometallics **2005,** *24,* 5937−5944

C-Metalated Diazoalkane Complexes of Platinum Based on PCP- and PCN-Type Ligands

Elena Poverenov,[†] Gregory Leitus,[‡] Linda J. W. Shimon,[‡] and David Milstein[*,†]

Department of Organic Chemistry and Unit of Chemical Research Support,
The Weizmann Institute of Science, Rehovot 76100, Israel

Received July 27, 2005

A series of the first C-metalated diazoalkane complexes of Pt, based on pincer-type PCN and PCP ligands ($PCP = C_6H_3[CH_2P(iPr)_2]_2$; $PCN = C_6H_3[CH_2P(tBu)_2](CH_2)_2N(CH_3)_2)$), with the general formula $(PCX)Pt[C(N_2)R]$ (**2**, X = N, R = Ph; **3**, X = N, R = $SiMe_3$; **5**, X = P, R = Ph) were prepared via direct nucleophilic attack of $RCN_2^-Li^+$ at the metal center. These remarkably stable complexes were characterized by ^1H, $^{31}P\{^1H\}$, and ^{13}C NMR and IR spectroscopy. Complex **2** was also characterized by single-crystal X-ray crystallography. Reactions of the C-metalated diazoalkane Pt complexes with Cu(I) (reported to catalyze decomposition of diazoalkanes) were strongly influenced by the nature of the pincer ligand. Bimolecular coupling to generate diphenylacetylene and (PCP)Pt−OTf (**6**) was observed in the case of the rigid PCP-based complex **5**, while the hemilabile PCN-based complex **2** was converted to an ylide-bridged dimeric structure, the formation of which was promoted by the decoordination of the ligand amine arm. In addition, formation of the stable metal-substituted azine-type binuclear complex **10**, generated by reaction of **2** with $Rh_2(OAc)_4$, is described.

Introduction

Reactions of organometallic complexes with diazoalkanes have attracted much attention, since diazoalkanes are useful substrates in the synthesis of carbene complexes, formed as a result of N_2 loss,[1] and in the generation of metal carbene intermediates in catalytic cyclopropanation and C−H activation reactions.[2] However, the diazo unit could also remain coordinated to the metal center, resulting in N- or C-bonded diazoalkane complexes. While a growing number of N-coordinated organometallic complexes have been reported and studied in connection with dinitrogen activation,[3] only few examples of C-coordinated complexes have been described. One of the reasons for the interest in C-metalated diazoalkanes is the potential for controlled release of N_2 to give reactive carbenoid species. Since carbene reactivity is strongly influenced by the nature of the LnM fragment,[4] α-metalation of diazoalkanes can allow tuning of their reactivity by variations in the metals and ligands. In addition, C-metalated diazo complexes may provide new pathways for the synthesis of organic and organometallic compounds. To the best of our knowledge, the relatively few reported C-metalated diazoalkane complexes include complexes of the metals Rh,[5] Pd,[6] Ni,[7] and Os.[8]

Bulky bis-chelating tridentate pincer-type ligands are effective in the stabilization of reactive species.[9] Using phosphine-based pincer-type ligands, stable complexes of carbene,[10] quinone methide,[11] phenoxonium,[12] xylylene,[13] metallaquinone,[14] and methylene arenium[15]

---

[*] To whom correspondence should be addressed. E-mail: david.milstein@weizmann.ac.il. Fax: 972-8-9344142.

[†] Department of Organic Chemistry.

[‡] Unit of Chemical Research Support.

(1) (a) Che, C. M.; Huang, J. S. *Coord. Chem. Rev.* **2002**, *231*, 151. (b) Cohen, R.; Rybtchinski, B.; Gandelman, M.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 6532. (c) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (d) Davies, H. M. L.; Autoulinakis, E. G. *J. Organomet. Chem.* **2001**, 47.

(2) (a) Maas, G. *Chem. Soc. Rev.* **2004**, *33*, 183. (b) Penoni, A.; Wanke, R.; Tollari, S.; Gallo, E.; Musella, D.; Ragaini, F.; Demartin, F.; Cenini, S. *Eur. J. Inorg. Chem.* **2003**, *7*, 1452. (c) Marko, I. E.; Kumamoto, T.; Giard, T. *Adv. Synth. Catal.* **2002**, *344*, 1063. (d) Lin, Y.-L.; Turos, E. *J. Organomet. Chem.* **2001**, *630*, 57.

(3) (a) Dartiguenave, M.; Menu, M. J.; Deydier, E.; Dartiguenave, Y.; Siebald, H. *Coord. Chem. Rev.* **1998**, 623. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800. (c) Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1978**, 749. (d) Claus, A. D.; Dimas, P. A.; Sharpley, J. R. *J. Organomet. Chem.* **1980**, *201*, C31. (e) Claus, A. D.; Sharpley, J. R. Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 7387. (f) Dimas, P. A.; Sharpley, J. R. *J. Organomet. Chem.* **1982**, *228*, C12. (g) Ortmann, D. A.; Weberndoerfer, B.; Ilg, K.; Laubender, M.; Werner, H. *Organometallics* **2002**, *21*, 2369. (h) Werner, H.; Mahr, N.; Wolf, J.; Fries, A.; Laubender, M.; Bleuel, E.; Garde, R.; Lahuerta, P. *Organometallics* **2003**, *22*, 3566.

(4) (a) Carter, E. A.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 2180. (b) Carter, E. A.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 4746.

(5) (a) Deydier, E.; Menu, M. J.; Dartiguenave, M.; Dartiguenave, Y.; Simard, M.; Beauchamp, A. L.; Brewer, J. C.; Gray, H. B. *Organometallics* **1996**, *15*, 1166. (b) Menu, M. J.; Desrosiers, P.; Dartiguenave, M.; Dartiguenave, Y.; Bertrand, G. *Organometallics* **1987**, *6*, 1822.

(6) (a) Murahashi, S. I.; Kitani, Y.; Hosokawa, T.; Miki, K.; Kasai, N. *J. Chem. Soc., Chem. Commun.* **1979**, 450. (b) Murahashi, S. I.; Kitani, Y.; Uno, T.; Hosokawa, T.; Miki, K.; Yonezawa, T.; Kasai, N. *Organometallics* **1986**, *5*, 356.

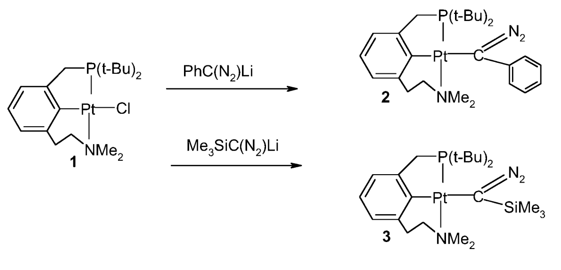
(7) Menu, M. J.; Konig, H.; Dartiguenave, M.; Dartiguenave, Y.; Klein, H. F. *J. Am. Chem. Soc.* **1990**, *112*, 5351.

(8) Gallo, M. A.; Jones, T. C.; Ricard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1984**, 1002.

(9) For recent reviews on pincer-type complexes, see: (a) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (b) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (c) Jensen, C. J. *Chem. Commun.* **1999**, 2443. (d) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837. (e) Vigalok, A.; Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798. (f) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 870. (g) Milstein, D. *Pure Appl. Chem.* **2003**, *75*, 2003. (h) Milstein, D.; Rybtchinski, B. *ACS Symp. Ser.* **2004**, *No. 885*, 70.

10.1021/om050637x CCC: $30.25

Scheme 1



have been synthesized. In addition, pincer-type ligands have been utilized in the stabilization of highly unsaturated cationic complexes.[16] With an interest in the generation of C-metalated diazo complexes with controllable properties, we have decided to utilize pincer-type ligands.

In this paper we report the synthesis of the first C-metalated diazo complexes of Pt. These complexes are based on hemilabile PCN and rigid PCP pincer-type systems. It is demonstrated that the reactivity of C-metalated diazoalkane complexes is strongly dependent on the pincer-ligand properties. In addition, formation of a metal-substituted azine compound is described.

Results and Discussion

Formation of C-Metalated Diazo Complexes Based on a Hemilabile PCN Ligand. The recently reported[17] complex **1**, based on the "long N-arm" hemilabile PCN ligand, was reacted with the *in situ* prepared lithiated diazo compound $PhCN_2^-Li^+$ in THF at −30 °C (Scheme 1). After 30 min the reaction mixture was warmed to room temperature, resulting in a red solution of (PCN)Pt[C(N$_2$)Ph] (**2**). The pure complex **2** was fully characterized by ^{31}P, ^{1}H, and ^{13}C NMR and IR spectroscopy. In $^{31}P\{^1H\}$ NMR it gives rise to a singlet at 63.11 ppm with Pt satellites (J_{Pt-P} = 4025 Hz), and in the $^{13}C\{^1H\}$ NMR spectrum the Pt[C(N$_2$)Ph] carbon appears as a singlet at 157.92 ppm and the ipso carbon exhibits a doublet at 149.99 ppm (J_{P-C} = 1 Hz). In the IR spectrum the diazo unit gives rise to absorption at 1962 cm^{-1}.

Yellow plates of complex **2** suitable for a single-crystal X-ray analysis were obtained by crystallization of **2** from a benzene/pentane solution at room temperature (Figure 1). Selected bond lengths and bond angles are given in Table 1. According to the X-ray data, complex **2** has a slightly distorted square planar structure. The Pt−C^1 bond length of 2.147 Å is slightly shorter than other reported Pt−C bond distances *trans* to aryl groups, which are usually close to 2.20 Å (2.187 Å for $C_6H_3[CH_2P(tBu)_2][CH_2CH_2N(Me)_2]PtCH_3$[17] or 2.186 Å for $C_6H_3[CH_2P(Ph)_2]_2PtCF_2CF_2CF_3$[18]). This might have a contribution to the high stability of complex **2**.

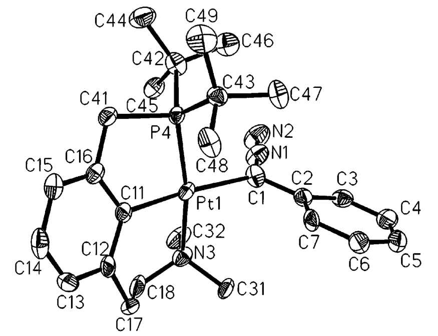
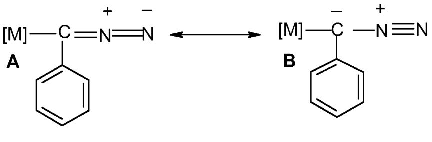


Figure 1. ORTEP view of a molecule of complex **2** at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complex 2

	Bond Lengths		
Pt(1)−C(1)	2.147(7)	C(1)−C(2)	1.469(11)
Pt(1)−N(3)	2.177(6)	N(1)−C(1)	1.297(10)
Pt(1)−P(4)	2.220(18)	N(1)−N(2)	1.144(10)
Pt(1)−C(11)	2.053(7)	C(2)−C(7)	1.398(10)
	Bond Angles		
C(1)−Pt(1)−N(3)	88.5(3)	C(1)−N(1)−N(2)	176.3(8)
C(1)−Pt(1)−P(4)	96.8(2)	N(1)−C(1)−C(2)	112.7(7)
C(11)−Pt(1)−N(3)	93.2(3)	N(1)−C(1)−Pt(1)	123.5(6)
C(11)−Pt(1)−P(4)	83.6(2)	C(2)−C(1)−Pt(1)	122.8(5)

The diazo CN$_2$ unit is almost linear (176.3°), and C−N (1.30 Å) and N−N (1.14 Å) bond lengths are similar to those usually observed for C-metalated diazoalkanes. However, in comparison with the corresponding bond lengths of the Pd(II) and Rh(I) complexes $PdCl(N_2CCO_2Et)(PPh_3)_2$ (C−N = 1.27 Å, N−N = 1.17 Å)[6a] and $Rh(N_2CSiMe_3)(PEt_3)_3$ (C−N =1.28 Å, N−N = 1.18 Å),[5a] it is noteworthy that complex **2** has a higher contribution of "C−N(single bond)−N−N(triple bond)" (structure **B**) than other C-metalated d^8 complexes.



The phenyldiazomethyl group is oriented in a 70° angle relative to the coordination plane, perhaps due to steric reasons. The presence of the bulky *tert*-butyl groups on the phosphine arm can result in repulsive interactions with the phenyl substituent. The diazo carbon of complex **2** exhibits sp^2 hybridization: N1−C1−C2 (112.7°), N1−C1−Pt1 (123.5°), and C2−C1−Pt1 (122.8°).

Another PCN-based platinum C-metalated diazo complex, bearing the bulky electron-donating Me$_3$Si substituent, was synthesized by the reaction of **1** with the

---

[10] (a) Gandelman, M.; Rybtchinski, B.; Ashkenazi, N.; Gauvin, R. M.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 5372. (b) Vigalok, A.; Milstein, D. *Organometallics* **2000**, *19*, 2061.

[11] Vigalok, A.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 7873.

[12] Vigalok, A.; Rybtchinski, B.; Gozin, Y.; Koblenz, T. S.; Ben-David, Y.; Rozenberg, H.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 15692.

[13] Vigalok, A.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 477.

[14] Ashkenazi, N.; Vigalok, A.; Parthiban, S.; Ben-David, Y.; Shimon, L. J. W.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 8797.

[15] (a) Vigalok, A.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 477. (b) Vigalok, A.; Rybtchinski, B.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 895. (c) Vigalok, A.; Milstein, D. *Organometallics* **2000**, *19*, 2341. (d) Gandelman, M.; Konstantinovski, L.; Rozenberg, H.; Milstein, D**.** *Chem. Eur. J.* **2003**, *9*, 2595.

[16] Gandelman, M.; Konstantinovski, L.; Rozenberg, H.; Milstein, D.; *Chem. Eur. J.* **2003**, *9*, 2595.

[17] Poverenov, E.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Ben-David, Y.; Milstein, D. *Chem. Eur. J.* **2004**, *10*, 4673.

[18] Hughes, R. P.; Williamson, A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **2001**, *20*, 4741.

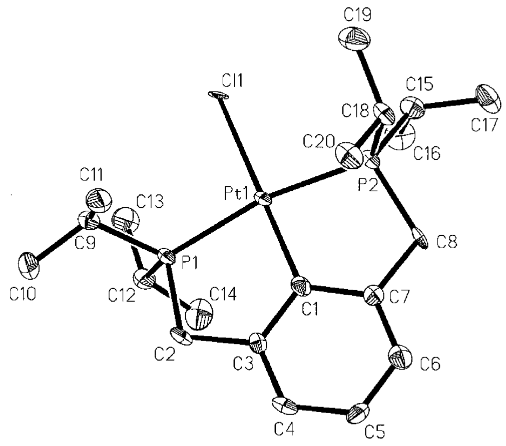
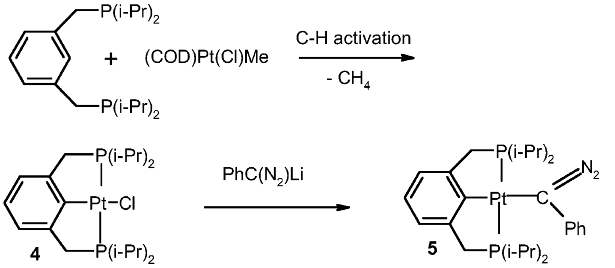


Figure 2. an ORTEP view of a molecule of complex **4** at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 2



in situ prepared $Me_3SiC(N_2)Li$ in THF at −30 °C (Scheme 1). Warming the reaction mixture to room temperature after 1 h revealed, on the basis of the $^{31}P\{^1H\}$ NMR spectrum, formation of the clean complex **3**. This complex was fully characterized by ^{31}P, ^1H, and ^{13}C NMR and IR spectroscopy. $^{31}P\{^1H\}$ NMR exhibits a singlet at 65.14 ppm with Pt satellites (J_{Pt-P} = 4166 Hz), and in the $^{13}C\{^1H\}$ NMR spectrum the Pt[C(N_2)-$SiMe_3$] carbon appears as a doublet at 155.94 ppm (J_{P-C} = 2 Hz), while the ipso carbon gives rise to a doublet at 149.60 ppm (J_{P-C} = 9 Hz). The CN_2 absorption in the IR spectrum was observed at 1956 cm^{-1}.

Formation of a C-Metalated Diazo Complex Based on a PCP Ligand. For this purpose, the new (PCP)PtCl complex **4** was first prepared. It was obtained as a result of C−H activation and methane elimination in the reaction of the PCP[19] ligand with 1 equiv of (COD)Pt(Me)Cl[20] (Scheme 2). The reaction mixture was heated in toluene at 140 °C for 12 h, resulting in a colorless solution, the $^{31}P\{^1H\}$ NMR of which revealed formation of complex **4**. Pure **4** was characterized by ^{31}P, ^1H, and ^{13}C NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits a singlet at 58.51 ppm with Pt satellites (J_{Pt-P} = 2858 Hz), and in the $^{13}C\{^1H\}$ NMR spectrum the ipso carbon gives rise to a triplet at 149.38 ppm (J_{P-C} = 11 Hz). X-ray-quality colorless crystals of complex **4** were obtained by recrystallization from pentane at room temperature. The single-crystal X-ray study reveals a slightly distorted square planar structure (Figure 2); the P−Pt−Cl angles are about 96°, while the P−Pt−C angles are approximately 84°. Selected angles and bond lengths are given in Table 2.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex 4

Bond Lengths			
Pt(1)−C(1)	2.006(6)	C(1)−C(3)	1.843(6)
Pt(1)−P(1)	2.275(17)	P(1)−C(12)	1.827(7)
Pt(1)−P(2)	2.183(17)	C(15)−C(17)	1.537(10)
Pt(1)−Cl(1)	2.436(14)	C(1)−C(7)	1.43(8)
Bond Angles			
C(1)−Pt(1)−P(1)	84.0 (18)	P(1)−N(1)−P(2)	167.4(5)
C(1)−Pt(1)−P(2)	83.6 (18)	C(1)−Pt(1)−Cl(1)	177.7(16)
P(1)−Pt(1)−Cl(1)	96.2(5)	C(9)−P(1)−Pt(1)	117.5(2)
P(2)−Pt(1)−Cl(1)	96.1(6)	C(8)−P(2)−Pt(1)	102.0(2)

Complex **4** was reacted with an *in situ* prepared THF solution of $PhCN_2^-Li^+$ at −30 °C. After 1 h the reaction mixture was warmed to reach room temperature, resulting in the formation of complex **5** (Scheme 2), which was isolated and characterized by ^{31}P, ^1H, and ^{13}C NMR and IR spectroscopy. In the $^{31}P\{^1H\}$ NMR spectrum **5** gives rise to a singlet at 56.20 ppm with Pt satellites (J_{Pt-P} = 2778 Hz), and in the $^{13}C\{^1H\}$ NMR spectrum the Pt[C(N_2)Ph] carbon is observed as a doublet at 166.35 ppm (J_{P-C} = 4 Hz) while the ipso carbon exhibits a triplet at 150.45 ppm (J_{P-C} = 1 Hz). The CN_2 absorption appears in the IR spectrum at 1968 cm^{-1}.

It is interesting to note that the diazo complexes **2**, **3**, and **5** are very stable and can be heated to more than 100 °C with no evidence of decomposition. This is quite remarkable, considering the fact that most of the diazoalkanes, excluding those bearing electron-withdrawing groups such as diazocarbonyls, are unstable. Apparently, α-metalation, as well as carbonyl group substitution,[21] stabilizes diazoalkanes due to the lowering of electron density on the diazo carbon.

Reactivity of C-Coordinated Diazoalkane Complexes. (a) Reactions with Cu(I). We were interested in studying the possibility of N_2 extrusion from the C-metalated Pt complexes and the effect of the pincer system on this process. Stable organic diazoalkane compounds undergo dinitrogen extrusion at noticeably lower temperatures in the presence of a catalyst, leading to synthetically useful reactions.[21] The development of catalysts for diazo decomposition began in the 1960s with the introduction of various copper compounds.[22] In the present research we decided to use the copper(I) triflate (Cu(OTf)) salt, which was introduced by Kochi and Salomon as a highly active catalyst for diazo decomposition.[23]

When the rigid PCP-based complex **5** was reacted with the complex Cu(OTf)(C_6H_6) in THF, decomposition of **5** was detected by the disappearance of the C=N=N signal in the IR spectrum and formation of a new complex **6**, as revealed by $^{31}P\{^1H\}$ NMR (Scheme 3). Complex **6** was identified spectrally as (PCP)Pt(OTf), and its structure was confirmed by an independent synthesis.

Complex **6** can be alternatively synthesized by the reaction of the corresponding methyl complex with triflic

---

(19) Rybtchinski, B.; Ben-David, Y.; Milstein, D. *Organometallics* **1997**, *16*, 3786.

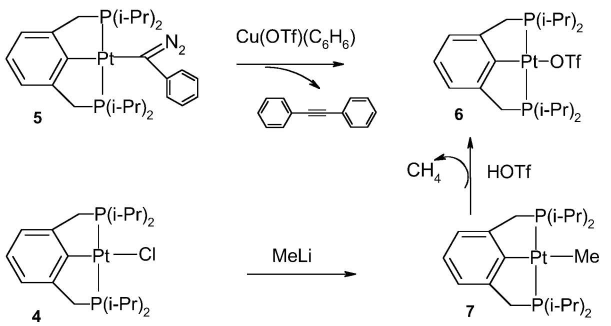
(20) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

(21) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911.

(22) (a) Moser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 1135. (b) Nozaki, H.; Moriuti, S.; Yamabe, M.; Noyori, R. *Tetrahedron Lett.* **1966**, 9. (c) Nozaki, H.; Moriuti, S.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1966**, 5239. (d) Corey, E. J.; Myers, A. G.; *Tetrahedron Lett.* **1984**, *25*, 3559. (e) Nugent, W. A.; Waller, F. J. *Synth. Commun*, **1988**, *18*, 61.

(23) (a) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300. (b) Salomon, R. G.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1972**, 559.

Scheme 3



acid (Scheme 3). When (PCP)PtCl (**4**) was reacted with an ethereal solution of MeLi at room temperature in THF, formation of (PCP)PtMe (**7**) was immediately observed. This complex gives rise to a singlet at 57.47 ppm with Pt satellites ($J_{\mathrm{Pt-P}}$ = 2902 Hz) in ^{31}P{^{1}H} NMR, and its Pt−Me group is observed at −18.95 ppm as a triplet ($J_{\mathrm{P-C}}$ = 8 Hz) in ^{13}C{^{1}H} NMR. Reaction of complex **7** with 1 equiv of triflic acid at −30° C in toluene, followed by warming to room temperature, led to formation of complex **6.** ^{31}P{^{1}H} NMR of **6** exhibits a singlet at 65.30 ppm with Pt satellites ($J_{\mathrm{Pt-P}}$ = 2897 Hz). In the ^{13}C{^{1}H} NMR spectrum the ipso carbon appears as a triplet at 149.37 ppm ($J_{\mathrm{P-C}}$ = 9 Hz), and in ^{19}F NMR the triflate anion is observed at −75.11 ppm as a broad singlet.

Apparently, reaction of complex **5** with Cu(I) results in dinitrogen loss and formation of a reactive carbenoid intermediate that undergoes bimolecular coupling to generate diphenylacetylene, which was detected by GC and GC/MS techniques. The resulting cationic [(PCP)-Pt]$^+$ species coordinates the triflate anion to give complex **6**.

In previous studies we have shown that hemilability of a pincer ligand can strongly affect the properties of its metal complex and can lead to unusual reactivity.[17,24] In the current study we have observed significant differences in the reactivity of the rigid PCP and hemilabile PCN-based diazo complexes. Thus, an analogous reaction of Cu(OTf)(C$_6$H$_6$) performed with the hemilabile PCN-based complex **2** led to a completely different type of product (Scheme 4). When **2** was reacted with the Cu(I) complex in THF, the C=N=N signal in the IR spectrum disappeared and formation of a new complex was revealed by ^{31}P{^{1}H} NMR. Workup yielded complex **8** as a green solid, which was stable for several hours at room temperature and for weeks at −20 °C. Its postulated structure is based on NMR and ES-MS spectroscopy. It exhibits a singlet at 105.79 ppm with Pt satellites ($J_{\mathrm{Pt-P}}$ = 2782 Hz) in ^{31}P{^{1}H} NMR, and in the ^{13}C{^{1}H} NMR spectrum, the two bridging ylide carbons, which are different because of the lack of a symmetry plane, appear as doublets at 156.72 ppm ($J_{\mathrm{P-C}}$ = 8 Hz) and at 156.51 ppm ($J_{\mathrm{P-C}}$ = 8 Hz). ES-MS spectroscopy shows signals at m/z^+ 1329.49 (weak peak, complex **8** [1180] + OTf [149]), 590.25 ($^1/_2$ of **8**), and 501.18 ((PCN)Pt).

In this case we believe that the unstable carbenoid intermediate **2′**, which may be formed as a result of N$_2$ extrusion, undergoes an intramolecular reaction with the labile N arm that dissociates from the Pt center. The resulting postulated ylide intermediate **2″** can undergo dimerization to generate complex **8** (Scheme 4). A similar mode of reactivity was observed with C-metalated diazoalkane complexes of Rh[5a] and Ni.[7] Upon photolysis of these complexes, dissociation of one of the monodentate phosphine ligands took place, followed by attack on the carbenoid intermediate and dimerization.

Interestingly, the binuclear complex **8** can be cleaved by reaction with triphenylphosphine to give products analogous to those obtained in the PCP case. Thus, addition of 1 equivalent of triphenylphosphine leads to immediate disappearance of the green color and formation of (PCN)Pt(OTf)[24] (**9**) and diphenylacetylene (Scheme 5). The PPh$_3$ remains unchanged. While the mechanism of dimer conversion to **9** is not clear, it is possible that phosphine coordination to Pt results in bridge cleavage, forming a carbenoid intermediate that undergoes dimerization to yield diphenylacetylene.

In the case of complex **5**, because of the strongly coordinated phosphine arms of the PCP ligand, there is no possibility of reaction of the carbenoid intermediate with the phosphine and the system is stabilized by a bimolecular reaction. Thus, by modification of the pincer ligand it is possible to modify the reactivity of diazoalkyl complexes.

(b) Reaction with Rh$_2$(OAc)$_4$. Decomposition of diazoalkane compounds mediated by dirhodium(II) tetraacetate, Rh$_2$(OAc)$_4$, is well-known,[21] and it was of interest to us to explore its reactivity with the metalated diazo complexes. Heating of complex **2** with Rh$_2$(OAc)$_4$ at 110 °C for 72 h resulted in formation of the novel complex **10** (Scheme 6). In a competing reaction (PCN)-Pt(OAc) (**11**) was also formed (ratio **10**:**11** = 1:1). Complex **11** was also independently and quantitatively generated by heating of (PCN)PtMe[17] with Rh$_2$(OAc)$_4$ at 110 °C for 72 h.

Complex **10** gives rise to a singlet at 62.68 ppm ($J_{\mathrm{P-Pt}}$ = 4222 Hz) in the ^{31}P{^{1}H} NMR spectrum, and in the ^{13}C{^{1}H} NMR spectrum it exhibits a singlet at 190.26 ppm and its ipso carbon is observed at 159.03 ppm as a doublet ($J_{\mathrm{P-C}}$ = 10 Hz). The former ^{13}C{^{1}H} NMR signal caused us to consider formation of an azine-type compound, since a similar downfield chemical shift (192.88 ppm, singlet) of the sp^2 *C*=N carbon was reported for the azine compound (Me$_3$Sn)(Ph)C=NN=C(Ph)(SnMe$_3$), generated by reaction of Me$_3$Sn[(C(N$_2$)Ph] with Rh$_2$(OAc)$_4$.[25] Our suggestion was supported by ES-MS spectroscopy, which exhibited a characteristic pattern of azine-type dimer: m/z^+ 1209.95 (complex **10** + 1), 1233.14 (**10** + 1 + Na$^+$), 1249.25 (**10** + 1 + K$^+$), 590.17 ($^1/_2$ of **10** − N$_2$). A possible mechanism of complex **10** formation is shown in Scheme 7. Reaction with rhodium acetate may lead to formation of an electrophilic Pt-substituted Rh carbene, which is attacked by the nucleophilic terminal nitrogen of another molecule of complex **2** to give the azine-type complex **10**.

Summary

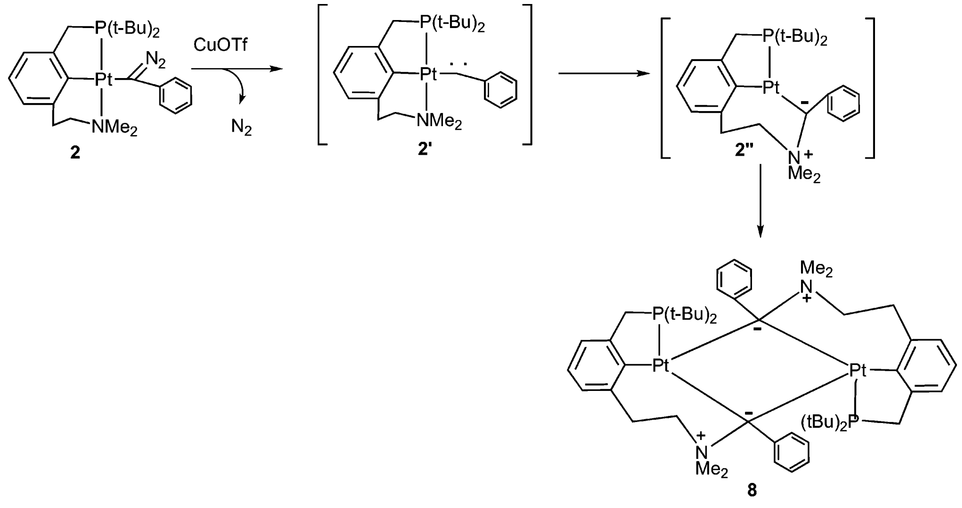
A series of the first C-coordinated diazoalkane complexes of Pt, based on pincer-type PCN and PCP ligands,

---

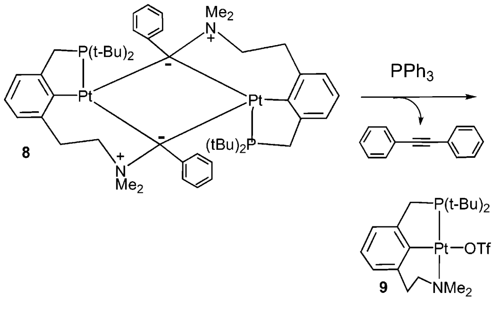
[24] Poverenov, E.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Ben-David, Y.; Milstein, D. *Organometallics* **2005**, *24*, 1082.

[25] Wheeler, M. T. Ph.D. Thesis, The Ohio State University, 1990.

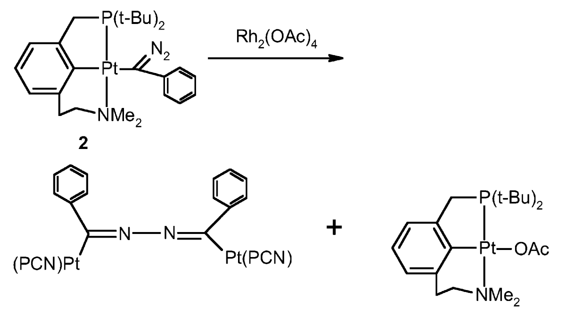
Scheme 4



Scheme 5



Scheme 6



was synthesized and fully characterized. These remarkably stable complexes were prepared by direct nucleophilic attack of $RCN_2^-Li^+$ on (PCX)PtCl complexes. Parallel reactivity studies of the hemilabile PCN-based complex **2** and of the analogous rigid PCP-based complex **5** with Cu(I) showed that the chemical behavior of the carbenoid moiety is strongly influenced by the nature of the pincer ligand. In the case of the rigid PCP-based complex, bimolecular coupling of the carbenoid moiety to generate diphenylacetylene and the complex (PCP)Pt−OTf was observed, while the PCN-based carbenoid was converted to the dimeric structure **8**, formation of which was induced by the hemilability of the amine ligand arm. Reaction of complex **2** with $Rh_2(OAc)_4$ led to formation of the stable azine-type complex **10**. Further reactivity of C-coordinated diazoalkane complexes based on different pincer-type ligands is under investigation.

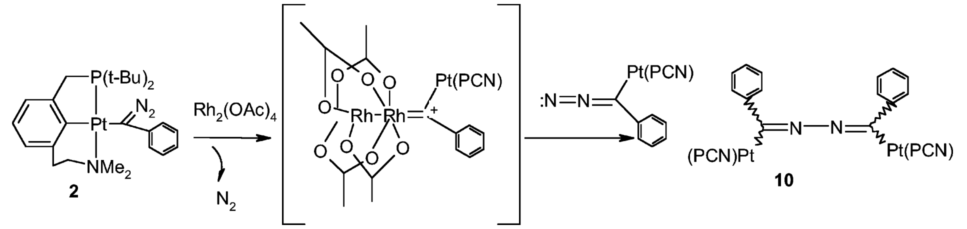
Experimental Section

General Procedures. All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with an MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. Commercially available reagents were used as received. The precursor $Pt(COD)(CH_3)Cl$ was prepared according to a literature procedure.[20] The NMR spectra were recorded at 250 (^1H), 101 (^{31}P), and 235 MHz (^{19}F) using a Bruker DPX 250 spectrometer, at 400 (^1H), 100 (^{13}C), 162 (^{31}P), and 376 MHz (^{19}F) using a Bruker AMX-400 NMR spectrometer, and at 500 (^1H), 126 (^{13}C), and 202 MHz (^{31}P) using a Bruker DPX 500 spectrometer. All spectra were recorded at 23 °C. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents (7.15 ppm, benzene; 2.04 ppm, acetone). In $^{13}C\{^1H\}$ NMR measurements the signals of C_6D_6 (128.0 ppm) and d_6-acetone (206.0 ppm) were used as a reference. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. ^{19}F NMR chemical shifts were referenced to C_6F_6 (−163 ppm). Screw-cap 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: s, singlet; d, doublet; t, triplet; m, multiplet.

Preparation of (PCN)Pt[C(N$_2$)Ph] (2). To a THF solution (1 mL) of $Me_3Sn[C(N_2)Ph]$ (45 mg, 0.16 mmol) at − 30 °C was added 100 μL of an nBuLi solution in hexane (1.6 M, 0.16 mmol) resulting in immediate appearance of the green color of $PhC(N_2)Li$. The resulting solution of $PhC(N_2)Li$ was added to a THF solution (1 mL) of complex **1**[17] (78 mg, 0.15 mmol) at −30 °C. After 30 min the mixture was heated to room temperature, resulting in a red solution. The $^{31}P\{^1H\}$ NMR spectrum revealed formation of complex **2**. The solvent was evaporated, and the complex was washed with pentane and dissolved in benzene. Benzene evaporation yielded 74 mg (0.12 mmol, 82% yield) of **2**. X-ray-quality yellow crystals were obtained from a benzene/pentane two-phase mixture at room temperature.

$^{31}P\{^1H\}$ NMR (C_6D_6): 63.11 (s, J_{P-Pt} = 4025 Hz). ^1H NMR (C_6D_6): 7.25 (d, J_{H-H} = 1 Hz, 1H, Ar), 7.23 (d, J_{H-H} = 1 Hz,

Scheme 7



1H, Ar), 7.22 (d, $J_{\mathrm{H-H}} = 1$ Hz, 1H, Ar), 6.90 (t, $J_{\mathrm{H-H}} = 1$ Hz, 2H, Ar), 6.88 (t, $J_{\mathrm{H-H}} = 1$ Hz, 2H, Ar), 6.87 (t, $J_{\mathrm{H-H}} = 1$ Hz, 1H, Ar),), 3.08 (m, 1H, CH$_2$C*H*$_2$N), 2.83 (m, 1H, CH$_2$C*H*$_2$N), 2.67 (d, $J_{\mathrm{P-H}} = 2$ Hz, 2H, ArC*H*$_2$P) 2.45 (d, $J_{\mathrm{P-H}} = 2$ Hz, 3H, NC*H*$_3$), 2.32 (d, $J_{\mathrm{H-P}} = 2$ Hz, 3H, NC*H*$_3$), 2.25 (m, 1H, C*H*$_2$-CH$_2$N), 1.84 (m, 1H, C*H*$_2$CH$_2$N), 1.27 (d, $J_{\mathrm{P-H}} = 14$ Hz, 9 H, P*tBu*), 0.88 (d, $J_{\mathrm{P-H}} = 14$ Hz, 9 H, P*tBu*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 157.92 (s, Pt−*C*=N$_2$), 149.99(d, $J_{\mathrm{P-C}} = 1$ Hz, ipso), 144.92 (s, Ar), 143.99 (s, Ar), 124.81 (s, Ar), 124.31 (s, Ar), 121.38 (s, Ar), 121.26 (s, Ar), 121.19 (s, Ar), 64.44 (s, CH$_2$*C*H$_2$N), 63.50 (s, *C*H$_2$CH$_2$N), 52.33 (d, $J_{\mathrm{P-C}} = 1$ Hz, N*C*H$_3$), 50.72 (d, $J_{\mathrm{P-C}} = 1$ Hz, N*C*H$_3$), 37.21 (d, $J_{\mathrm{P-C}} = 34$ Hz, Ar*C*H$_2$P), 35.00 (d, $J_{\mathrm{P-C}} = 30$ Hz, P*C*(CH$_3$)$_3$), 34.59 (d, $J_{\mathrm{P-C}} = 30$ Hz, P*C*(CH$_3$)$_3$), 29.61 (d, $J_{\mathrm{P-C}} = 4$ Hz, PC(*C*H$_3$)$_3$), 29.31 (d, $J_{\mathrm{P-C}} = 4$ Hz, PC-(*C*H$_3$)$_3$). IR (film): ν(Pt−*C*=*N*=*N*) 1962 cm^{-1}. Anal. Found (calcd for $C_{26}H_{38}N_3PPt$): C, 50.27 (50.43); H, 6.14 (6.03).

X-ray Structural Analysis of 2. Complex **2** was crystallized from a benzene/pentane two-phase mixture at room temperature to give yellow crystals. Crystal data: $C_{26}H_{38}N_3PPt$, yellow, plate, 0.3 × 0.1 × 0.1 mm^3, triclinic, $P\bar{1}$ (No. 2), $a = 9.004(2)$ Å, $b = 11.345(2)$ Å, $c = 14.201(3)$ Å, $\alpha = 72.53(3)°$, $\beta = 88.51(3)°$, $\gamma = 77.85(3)°$ from 20 degrees of data, $T = 120(2)$ K, $V = 1232.5(4)$ Å^3, $Z = 2$, fw = 618.65, $D_c = 1.667$ Mg/m^3, $\mu = 5.774$ mm^{-1}. Data collection and treatment: Nonius KappaCCD diffractometer, Mo Kα ($\lambda = 0.710\,73$ Å), graphite monochromator, 17 632 reflections collected, $-11 < h < 11$, $-12 < k < 12$, $0 < l < 17$, frame scan width 1.0°, scan speed 1° per 100 s, typical peak mosaicity 2.08°, 3542 independent reflections ($R_{\mathrm{int}} = 0.057$). The data were processed with Denzo-Scalepack. Solution and refinement: structure solved by direct methods with SHELXS-97, full-matrix least-squares refinement based on F^2 with SHELXL-97, 288 parameters with 0 restraints, final R1 = 0.0439 (based on F^2) for data with $I > 2\sigma(I)$ and R1 = 0.0515 on all 4931 reflections, wR2 = 0.0938, goodness of fit on F^2 1.019, largest electron density peak 1.629 e/Å^3.

Formation of (PCN)Pt[C(N$_2$)SiMe$_3$] (3). To a THF solution (0.5 mL) of Me$_3$Si(CN$_2$)H (80 μL of a 2 M solution in toluene, 0.16 mmol) at − 30 °C was added 107 μL of a MeLi solution in ether (1.5 M, 0.16 mmol), and Me$_3$SiCN$_2$Li was immediately formed. The solution of the in situ prepared Me$_3$SiC(N$_2$)Li was added to a THF solution (1 mL) of (PCN)PtCl complex (78 mg, 0.15 mmol) at − 30 °C. After 1 h the mixture was heated to room temperature and the ^{31}P{^{1}H} NMR spectrum revealed the formation of clean complex **3**. The solvent was evaporated, and the complex was extracted with pentane. Pentane evaporation yielded 83 mg (0.13 mmol, 89% yield) of complex **3**.

^{31}P{^{1}H} NMR (C$_6$D$_6$): 65.14 (s, $J_{\mathrm{P-Pt}} = 4166$ Hz). ^{1}H NMR (C$_6$D$_6$): 7.03 (t, $J_{\mathrm{H-H}} = 6$ Hz, 1H, Ar), 6.89 (d, $J_{\mathrm{H-H}} = 6$ Hz, 1H, Ar), 6.87 (d, $J_{\mathrm{H-H}} = 6$ Hz, 1H, Ar), 3.11 (m, 1 H, CH$_2$C*H*$_2$N), 2.78 (m, 1 H, CH$_2$C*H*$_2$N), 2.67 (d, $J_{\mathrm{P-H}} = 2$ Hz, 2H, ArC*H*$_2$P) 2.62 (d, $J_{\mathrm{P-H}} = 2$ Hz, 3H, NC*H*$_3$), 2.51(d, $J_{\mathrm{P-H}} = 2$ Hz, 3H, NC*H*$_3$), 2.24 (m, 1H, C*H*$_2$CH$_2$N), 1.89 (m, 1H, C*H*$_2$CH$_2$N), 1.42 (d, $J_{\mathrm{P-H}} = 14$ Hz, 9 H, P*tBu*), 1.00 (d, $J_{\mathrm{P-H}} = 14$ Hz, 9 H, P*tBu*), 0.43 (s, 9 H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 155.94 (d, $J_{\mathrm{P-C}} = 2$ Hz, Pt−*C*=N$_2$), 149.60 (d, $J_{\mathrm{P-C}} = 9$ Hz, ipso), 144.17 (s, Ar), 125.42 (s, Ar), 124.47 (s, Ar), 123.61 (s, Ar), 121.00 (d, $J_{\mathrm{P-C}} = 16$ Hz, Ar), 67.54 (s, CH$_2$*C*H$_2$N), 64.44 (s, *C*H$_2$CH$_2$N), 52.25 (d, $J_{\mathrm{P-C}} = 1$ Hz, N*C*H$_3$), 49.52 (d, $J_{\mathrm{P-C}} = 1$ Hz, N*C*H$_3$), 36.90 (d, $J_{\mathrm{P-C}} = 35$ Hz, Ar*C*H$_2$P), 34.53 (d, $J_{\mathrm{P-C}} = 32$ Hz, P*C*(CH$_3$)$_3$), 34.16 (d, $J_{\mathrm{P-C}} = 30$ Hz, P*C*(CH$_3$)$_3$), 29.76 (d, $J_{\mathrm{P-C}} = 3$ Hz, PC(*C*H$_3$)$_3$), 28.99 (d, $J_{\mathrm{P-C}} = 3$ Hz, PC(*C*H$_3$)$_3$), 0.17 (s, Si(*C*H$_3$)$_3$) (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT). IR (film): ν(Pt−*C*=*N*=*N*) 1956 cm^{-1}. Anal. Found (calcd for $C_{23}H_{42}N_3PSiPt$): C, 45.08 (44.92); H, 6.87 (6.83).

Formation of (PCP)PtCl (4). To a toluene solution (3 mL) of the ligand C$_6$H$_3$(P(iPr)$_2$)$_2$ (110 mg, 0.33 mmol) was added 106 mg (0.30 mmol) of (COD)Pt(Cl)CH$_3$. The reaction mixture was heated at 140 °C for 12 h, resulting in a colorless solution. ^{31}P{^{1}H} NMR revealed formation of complex **4**. The solvent was evaporated, and the complex was washed with pentane and dissolved in benzene. After benzene evaporation 144 mg (0.26 mmol, 85% yield) of **4** was obtained.

^{31}P{^{1}H} NMR (C$_6$D$_6$): 58.51 (s, $J_{\mathrm{P-Pt}} = 2858$ Hz). ^{1}H NMR (C$_6$D$_6$): 7.10 (t, $J_{\mathrm{H-H}} = 7$ Hz, 1H, Ar), 6.85 (d, $J_{\mathrm{H-H}} = 7$ Hz, 2H, Ar), 2.70 (t, $J_{\mathrm{P-H}} = 4$ Hz, 4H, P(C*H*(CH$_3$)$_2$)$_2$), 2.19 (m, 4H, ArC*H*$_2$P), 1.35 (dd, $J_{\mathrm{P-H}} = 7$ Hz, $J_{\mathrm{P-H}} = 15$ Hz, 12 H, P(CH-(C*H*$_3$)$_2$)), 0.86 (dd, $J_{\mathrm{P-H}} = 7$ Hz, $J_{\mathrm{P-H}} = 15$ Hz, 12 H, P(CH-(C*H*$_3$)$_2$)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 149.38 (t, $J_{\mathrm{P-C}} = 11$ Hz, ipso), 128.29 (s, Ar), 124.18 (s, Ar), 122.50 (s, Ar), 122.43 (s, Ar), 122.35 (s, Ar), 33.34 (t, $J_{\mathrm{P-C}} = 15$ Hz, Ar*C*H$_2$P), 23.95 (t, $J_{\mathrm{P-C}} = 14$ Hz, P(*C*H(CH$_3$)$_2$)$_2$), 18.42 (t, $J_{\mathrm{P-C}} = 2$ Hz, P(CH(*C*H$_3$)$_2$)$_2$), 17.78 (t, $J_{\mathrm{P-C}} = 12$ Hz, P(*C*H(CH$_3$)$_2$)$_2$ (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT). Anal. Found (calcd for $C_{20}H_{35}P_2PtCl$): C, 42.21 (42.29); H, 6.13 (6.17).

X-ray Structural Analysis of 4. Complex **4** was crystallized from a pentane solution at room temperature to give white/colorless crystals. Crystal data: $(C_{20}H_{35}Cl_{1}P_{2}Pt)_2$, white/colorless, 1.0 × 0.8 × 0.2 mm^3, triclinic, $P\bar{1}$ (No. 2), $a = 11.148(2)$ Å, $b = 13.935(3)$ Å, $c = 14.683(3)$ Å, $\alpha = 78.16(3)°$, $\beta = 82.35(3)°$, $\gamma = 89.33(3)°$ from 20 degrees of data, $T = 120(2)$ K, $V = 2212.3(8)$ Å^3, $Z = 4$, fw = 567.96, $D_c = 1.705$ Mg/m^3, $\mu = 6.608$ mm^{-1}. Data collection and treatment: Nonius KappaCCD diffractometer, Mo Kα ($\lambda = 0.710\,73$ Å), graphite monochromator, 43 811 reflections collected, $-12 < h < 13$, $-15 < k < 16$, $0 < l < 17$, frame scan width 1.0°, scan speed 1° per 30 s, typical peak mosaicity 0.535°, 11 008 independent reflections ($R_{\mathrm{int}} = 0.117$). The data were processed with Denzo-Scalepack. Solution and refinement: structure solved by direct methods with SHELXS, full-matrix least-squares refinement based on F^2 with SHELXL-97, 449 parameters with 0 restraints, final R1 = 0.0378 (based on F^2) for data with $I > 2\sigma(I)$ and R1 = 0.0508 on 6834 reflections, wR2 = 0.1104, goodness of fit on F^2 = 1.043, largest electron density peak 2.047 e/Å^3.

Formation of (PCP)Pt[C(N$_2$)Ph] (5). A solution of in situ prepared (as described above, in the preparation of complex **2**) PhCN$_2$Li (0.17 mmol) was added to a THF solution (1 mL) of complex **4** (85 mg, 0.15 mmol) at −30 °C. After 1 h the mixture was warmed to room temperature, resulting in a red solution. The ^{31}P{^{1}H} NMR spectrum revealed formation of clean complex **5**. The solvent was evaporated, and the complex was washed with pentane and dissolved in benzene. Benzene evaporation yielded 78 mg (0.12 mmol, 80% yield) of **5**.

^{31}P{^{1}H} NMR (C$_6$D$_6$): 56.20 (s, $J_{\mathrm{P-Pt}} = 2778$ Hz). ^{1}H NMR (C$_6$D$_6$): 7.63 (d, $J_{\mathrm{H-H}} = 1$ Hz, 1H, Ar), 7.51 (d, $J_{\mathrm{H-H}} = 1$ Hz, 1H, Ar), 7.27 (s, 2 H, Ar), 7.25 (s, 1H, Ar), 6.92 (t, $J_{\mathrm{H-H}} = 2$ Hz, 1H, Ar), 6.87 (d, $J_{\mathrm{H-H}} = 2$ Hz, 1H, Ar), 6.80 (t, $J_{\mathrm{H-H}} = 2$

Hz, 1H, Ar), 2.93 (t, J_{P-H} = 4 Hz, 4H, P(C*H*(CH$_3$)$_2$)$_2$), 1.97 (m, 4H, ArC*H*$_2$P), 1.05 (dd, J_{P-H} = 6 Hz, J_{P-H} = 8 Hz, 12 H, P(CH(C*H*$_3$)$_2$)), 0.83 (dd, J_{P-H} = 6 Hz, J_{P-H} = 8 Hz, 12 H, P(CH(C*H*$_3$)$_2$)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 166.35 (d, J_{P-C} = 4 Hz, Pt−*C*=N$_2$), 150.45 (t, J_{P-C} = 1 Hz, ipso), 146.46 (s, Ar), 125.64 (s, Ar), 125.08 (s, Ar), 124.90 (s, Ar), 121.75 (t, J_{P-C} = 3 Hz, Ar), 120.92 (s, Ar), 36.53 (t, J_{P-C} = 16 Hz, Ar*C*H$_2$P), 25.02 (t, J_{P-C} = 15 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 18.10 (t, J_{P-C} = 1 Hz, P(CH(*C*H$_3$)$_2$)$_2$), 17.73 (t, J_{P-C} = 4 Hz, P(*C*H(CH$_3$)$_2$)$_2$. IR (film): ν(Pt−*C*=*N*$_2$) 1968 cm^{-1}. Anal. Found (calcd for C$_{27}$H$_{40}$N$_2$P$_2$Pt): C, 49.84 (49.42); H, 6.14 (6.16); N, 4.26 (4.31).

Formation of (PCP)Pt−OTf (6). To a toluene solution (1 mL) of complex **7** (40 mg, 0.073 mmol) was added 1 equiv of HOTf (6.5 μL, 0.073 mmol) at −30 °C. After 3 h the solution was warmed to room temperature and the solvent was evaporated. Complex **6** was washed with pentane and dissolved in benzene. Benzene evaporation yielded 43 mg (0.063 mmol, 87% yield) of complex **6**.

^{31}P{^{1}H} NMR (C$_6$D$_6$): 65.30 (s, J_{P-Pt} = 2897 Hz). ^{1}H NMR (C$_6$D$_6$): 6.96 (t, J_{H-H} = 3 Hz, 1H, Ar), 6.80 (d, J_{H-H} = 3 Hz, 2H, Ar), 2.51 (t, J_{P-H} = 4 Hz, 4H, ArC*H*$_2$P), 2.30 (m, 4H, P(C*H*(CH$_3$)$_2$)$_2$), 1.31 (dd, J_{P-H} = 10 Hz, J_{P-H} = 8 Hz, 12 H, P(CH(C*H*$_3$)$_2$)), 0.77 (dd, J_{P-H} = 8 Hz, J_{P-H} = 7 Hz, 12 H, P(CH(C*H*$_3$)$_2$)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 149.37 (t, J_{P-C} = 9 Hz, ipso), 127.45 (s, Ar), 125.48 (s, Ar), 122.88 (t, J_{P-C} = 9 Hz, Ar), 122.81 (s, Ar), 31.91 (t, J_{P-C} = 15 Hz, Ar*C*H$_2$P), 24.68 (t, J_{P-C} = 15 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 18.57 (t, J_{P-C} = 3 Hz, P(CH(*C*H$_3$)$_2$)$_2$), 17.81 (s, PtSO$_3$*C*F$_3$). ^{19}F NMR (C$_6$D$_6$): −75.11 (s, Pt−SO$_3$C*F*$_3$). Anal. Found (calcd for C$_{21}$H$_{35}$P$_2$PtO$_3$SF$_3$): C, 36.81 (37.00); H, 5.12 (6.14).

Synthesis of (PCP)Pt−Me (7). To a toluene solution (1 mL) of complex **4** (30 mg, 0.053 mmol) was added 58 μL (0.088 mmol) of a 1.5 M MeLi solution in ether, and formation of complex **7** was immediately revealed by ^{31}P{^{1}H} NMR. The solvent was evaporated, and complex **7** was extracted with pentane. Solvent evaporation yielded 27 mg (0.050 mmol, 95% yield) of complex **7**. This complex was unstable under high vacuum, and an acceptable elemental analysis could not be obtained.

^{31}P{^{1}H} NMR (C$_6$D$_6$): 57.47 (s, J_{P-Pt} = 2902 Hz). ^{1}H NMR (C$_6$D$_6$): 7.14 (bs, 2 H, Ar), 7.03 (bs, 1H, Ar), 2.51 (t, J_{P-H} = 4 Hz, 4H, ArC*H*$_2$P), 2.30 (m, 4H, P(C*H*(CH$_3$)$_2$)$_2$), 1.31 (dd, J_{P-H} = 6 Hz, J_{P-H} = 8 Hz, 12 H, P(CH(C*H*$_3$)$_2$)), 0.77 (dd, J_{P-H} = 6 Hz, J_{P-H} = 8 Hz, 12 H, P(CH(C*H*$_3$)$_2$)), the PtC*H*$_3$ signal is obscured under the P(CH(C*H*$_3$)$_2$ signal pattern. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 149.40 (t, J_{P-C} = 7 Hz, ipso), 128.52 (s, Ar), 123.44 (s, Ar), 121.21 (s, Ar), 121.14 (s, Ar), 122.07 (s, Ar), 38.72 (t, J_{P-C} = 16 Hz, Ar*C*H$_2$P), 24.03 (t, J_{P-C} = 14 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 18.50 (t, J_{P-C} = 3 Hz, P(CH(*C*H$_3$)$_2$)$_2$), 17.90 (t, J_{P-C} = 4 Hz, P(CH(*C*H$_3$)$_2$)$_2$), −18.95 (s, J_{Pt-C} = 8 Hz, Pt−*C*H$_3$) (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT).

Reaction of (PCP)Pt[C(N$_2$)Ph] (5) with Cu(OTf)(C$_6$H$_6$). When a red THF solution (0.5 mL) of complex **5** (40 mg, 0.068 mmol) was reacted with a THF solution (0.5 mL) of Cu(OTf)(C$_6$H$_6$) (34 mg 0.068 mmol), the red color immediately disappeared and the solution became brown. ^{31}P{^{1}H} NMR revealed formation of (PCP)Pt(OTf) (**6**), while signals of the CN$_2$ group in the IR spectrum disappeared. Formation of diphenylacetylene was observed by GC and CG/MS. Complex **6** was characterized by NMR and ES-MS spectroscopy, and its structure was also confirmed by independent synthesis. MS: *m*/*z*$^+$ 532.48 (M − OTf) (calcd 532.16), 148.82 (OTf) (calcd 149.07). The NMR data are identical with those reported above in the independent synthesis procedure.

Reaction of (PCN)Pt[C(N$_2$)Ph] (2) with Cu(OTf)(C$_6$H$_6$). Formation of Complex 8. To a THF solution (1 mL) of complex **2** (40 mg, 0.065 mmol) was added a THF solution (1 mL) of Cu(OTf)(C$_6$H$_6$) (32 mg, 0.065 mmol). The solution immediately became green, and ^{31}P{^{1}H} NMR revealed formation of a new complex, while the CN$_2$ absorption in the IR spectrum disappeared. The solvent was evaporated, and the green solid was washed with pentane and benzene and dissolved in THF. Evaporation of THF yielded 31 mg (0.053 mmol, 82% yield) of complex **8**. NMR measurements have been performed at −30 °C, since decomposition of complex **8** starts after several hours at room temperature.

^{31}P{^{1}H} NMR (d_6-acetone): 105.79 (s, J_{P-Pt} = 2782 Hz). ^{1}H NMR (C$_6$D$_6$): the aromatic and ligand arms region is unresolved; 1.16 (d, J_{P-H} = 6 Hz, 9 H, P(tBu)$_2$), 1.09 (d, J_{P-H} = 6 Hz, 9 H, P(tBu)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 156.72 (d, J_{P-C} = 8 Hz, Pt−*C*−Pt), 156.51 (d, J_{P-C} = 8 Hz, Pt−*C*−Pt), 148.44 (s, ipso), 146.87 (s, ipso), 145.25 (s, Ar), 143.82 (s, Ar), 143.25 (s, Ar), 141.10 (s, Ar), 138.27 (s, Ar), 136.49 (s, Ar), 134.13 (s, Ar), 133.76 (s, Ar), 132.29 (s, Ar), 132.02 (s, Ar), 130.90 (s, Ar), 130.86 (s, Ar), 130.73 (s, Ar), 130.57 (s, Ar), 130.49 (s, Ar), 130.25 (s, Ar), 129.97 (s, Ar), 129.88 (s, Ar), 129.57 (s, Ar), 128.98 (s, Ar), 128.87 (s, Ar), 126.81 (s, Ar), 64.67 (s, ArCH$_2$*C*H$_2$N), 63.68 (s, ArCH$_2$*C*H$_2$N), 59.65 (s, Ar*C*H$_2$CH$_2$N), 59.54 (s, Ar*C*H$_2$CH$_2$N), 50.79 (s, N(*C*H$_3$)$_2$), 50.72 (s, N(*C*H$_3$)$_2$), 43.63 (d, J_{P-C} = 42 Hz, Ar*C*H$_2$P), 43.57 (d, J_{P-C} = 42 Hz, Ar*C*H$_2$P), 39.65 (d, J_{P-C} = 16 Hz, P(*C*(CH$_3$)$_3$), 39.05 (d, J_{P-C} = 30 Hz, P(*C*(CH$_3$)$_3$), 28.97 (d, J_{P-C} = 5 Hz, P(C(*C*H$_3$)$_3$). ES-MS: *m*/*z*$^+$ 1329.49 (M + OTf, weak peak) (calcd 1329.8), 590.25 (^{1}/$_2$ M) (calcd 590.35), 501.18 (PCNPt) (calcd 501.35).

Reaction of Complex 8 with PPh$_3$. When a THF solution (0.5 mL) of complex **8** (40 mg, 0.068 mmol for the monomeric unit) was reacted with a THF solution (0.5 mL) of PPh$_3$ (18 mg, 0.068 mmol), the green color immediately disappeared and the solution became brown. ^{31}P{^{1}H} NMR revealed formation of (PCN)Pt(OTf) (**9**), which was characterized by NMR, showing data identical with those of the reported compound,[24] and formation of diphenylacetylene was detected by GC.

Reaction of (PCN)Pt[C(N$_2$)Ph] (2) with Rh$_2$(OAc)$_4$. Formation of ({PCN}Pt)(Ph)C=NN=C(Ph)(Pt{PCN}) (10). To a toluene solution (1 mL) of (PCN)Pt[C(N$_2$)Ph] (**2**; 20 mg, 0.035 mmol) was added 14 mg (0.035 mmol) of Rh$_2$(OAc)$_4$, and the reaction mixture was heated at 110 °C for 72 h. The ^{31}P{^{1}H} NMR spectrum revealed the disappearance of complex **2** and formation of two new complexes, (PCN)Pt(OAc) (**11**; structurally confirmed by independent synthesis) and [(PCN)PtPhCN]$_2$ (**10**). The solvent was evaporated, and the gray solid was washed with pentane and dissolved in benzene. Solvent evaporation yielded **10** in 50% yield according to the ^{31}P{^{1}H} NMR of the mixture.

Selected NMR data for complex **10** are as follows. ^{31}P{^{1}H} NMR (C$_6$D$_6$): 62.68 (s, J_{P-Pt} = 4222 Hz). ^{1}H NMR (C$_6$D$_6$): 7.12 (d, J_{H-H} = 7 Hz, 2 H, Ar), 7.07 (d, J_{H-H} = 7 Hz, 2H, Ar), 6.81 (d, J_{H-H} = 7 Hz, 1H, Ar), 6.61 (t, J_{H-H} = 5 Hz, 1H, Ar), 6.52 (t, J_{H-H} = 5 Hz, 1H, Ar), 6.45 (d, J_{H-H} = 5 Hz, 1H, Ar), 1.30 (d, J_{P-H} = 14 Hz, 18H, P(tBu)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 190.26 (s, Pt−*C*=N$_2$), 159.03 (d, J_{P-C} = 10 Hz, ipso), 142.47 (s, Ar), 139.65 (s, Ar), 139.40 (s, Ar), 139.15 (s, Ar), 137.82 (s, Ar), 132.08 (d, J_{P-C} = 5 Hz, Ar), 130.75 (s, Ar), 125.12 (s, Ar), 124.15 (s, Ar), 63.49 (s, ArCH$_2$*C*H$_2$N), 63.49 (s, ArCH$_2$*C*H$_2$N), 49.02 (s, N(*C*H$_3$)$_2$), 49.00 (s, N(*C*H$_3$)$_2$), 34.49 (d, J_{P-C} = 50 Hz, Ar*C*H$_2$P), 33.51 (d, J_{P-C} = 50 Hz, P(*C*(CH$_3$)$_3$), 28.95 (d, J_{P-C} = 5 Hz, P(C(*C*H$_3$)$_3$). ES-MS: *m*/*z*$^+$ 1209.95 (M + 1) (calcd 1209.71), 1233.14 (M + 1 + Na$^+$) (calcd 1232.70), 1249.25 (M + 1 + K$^+$) (calcd 1248.81), 590.17 (^{1}/$_2$ M − N$_2$) (calcd 590.35).

Synthesis of (PCN)Pt(OAc) (11). A toluene solution (2 mL) of (PCN)PtCH$_3$[17] (35 mg, 0.068 mmol) and Rh$_2$(OAc)$_4$ (30 mg, 0.068 mmol) was heated at 110 °C for 72 h. The ^{31}P{^{1}H} NMR spectrum revealed complete conversion to complex **11**. The solvent was evaporated, and the gray solid was washed with pentane and was dissolved in benzene. Solvent evaporation yielded 33 mg (0.059 mmol, 87% yield) of **11**. This complex was unstable under high vacuum, and an acceptable elemental analysis could not be obtained.

^{31}P{^{1}H} NMR (C$_6$D$_6$): 64.18 (s, J_{P-Pt} = 4175 Hz). ^{1}H NMR (C$_6$D$_6$): 7.08 (t, J_{H-H} = 3 Hz, 1H, Ar), 7.01(d, J_{H-H} = 3 Hz, 1H, Ar), 6.76 (d, J_{H-H} = 3 Hz, 1H, Ar), 2.69 (m, 2 H, CH$_2$C*H*$_2$N), 2.68 (d, J_{P-H} = 9 Hz, 2H, ArC*H*$_2$P), 2.52 (s, 3H, NC*H*$_3$), 2.51

(s, 3H, NCH_3), 2.26 (s, 3 H, CO_2CH_3), 1.23 (d, J_{P-H} = 13 Hz, 18 H, P*tBu*). $^{13}C\{^1H\}$ NMR (C_6D_6): 175.08 (s, CO_2CH_3), 150.81 (d, J_{P-C} = 1 Hz, ipso), 143.30 (s, Ar), 124.73 (s, Ar), 123.80 (s, Ar), 121.64 (s, Ar), 121.51 (s, Ar), 63.76 (s, CH_2CH_2N), 63.76 (s, CH_2CH_2N), 49.66 (s, NCH_3), 49.64 (s, NCH_3), 48.85 (d, J_{P-C} = 40 Hz, ArCH_2P), 36.21 (s, CO_2CH_3), 34.27 (d, J_{P-C} = 25 Hz, P$C(CH_3)_3$), 29.05 (d, J_{P-C} = 3 Hz, P$C(CH_3)_3$. IR (film): ν(Pt−C=O(OCH_3)) 1623 cm^{-1}.

Acknowledgment. This work was supported by the Israel Science Foundation, Jerusalem, Israel, by the DIP program for German-Israeli cooperation, and by the Helen and Martin Kimmel Center for Molecular Design. D.M. is the holder of the Israel Matz Professorial Chair of Organic Chemistry.

Supporting Information Available: CIF files containing X-ray crystallographic data for complexes **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050637X