Carbon−Carbon Bond Activation in Pt(0)−Diphenylacetylene Complexes Bearing Chelating P,N- and P,P-Ligands

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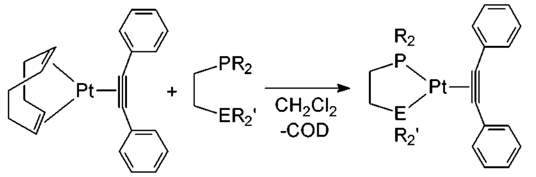
The cleavage of C−C bonds under mild conditions is currently an active research area in organometallic chemistry due to its potential application in the petroleum industry. Oxidative addition of C−C bonds to metal centers often relies on relief of ring strain or attainment of aromaticity, although the activation of an unstrained C−C bond has been achieved in the presence of highly reactive species, by forcing the target molecule into close proximity to the metal or by the formation of strong M−aryl bonds.[1,2]

We report here on the synthesis of various Pt(0)−diphenylacetylene complexes bearing chelating P,N- or P,P-ligands and on the cleavage of the C(sp^2)−C(sp) bond in diphenylacetylene. The η^2-alkyne complexes were quantitatively converted into the oxidative addition products under photolytic conditions. While carbon−alkyne C−C cleavage has been reported in a few isolated cases,[3] aryl−alkyne cleavage is quite difficult.[4]

Reaction of (COD)Pt(PhC≡CPh)[5] (**1**) with 1 equiv of (diisopropylphosphino-dimethylamino)ethane[6] (PN, **2**) in CH_2Cl_2 afforded the η^2-alkyne complex (PN)Pt(PhC≡CPh) (**3**) as a yellow, air- and moisture-sensitive solid in high yield after recrystallization from pentane/CH_2Cl_2 (eq 1). The $^{31}P\{^1H\}$ NMR spectrum of **3** in C_6D_6 displayed a singlet with Pt-satellites at δ = 65.8 ppm ($^1J_{Pt-P}$ = 3647 Hz).



(1)

1 **2, 5, 6**

E = N, R = iPr, R'= Me: **3**
E = P, R = R'= iPr: **7**
E = P, R = R'= Cy: **8**

A solution of **3** in C_6D_6 was irradiated with UV light,[7] and the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After 2 h the formation of a new species was observed. Within 45 h **3** was quantitatively converted into the product (**4**) which was obtained as a colorless solid after recrystallization. The $^{31}P\{^1H\}$ NMR spectrum of **4** showed a singlet at δ = 49.8 ppm with Pt-satellites ($^1J_{Pt-P}$ = 2697 Hz). In the ^1H NMR spectrum resonances were observed for two unique phenyl groups. In particular, platinum satellites for only one set of ortho phenyl protons were detected, which is characteristic for a phenyl group σ-bonded to a platinum center. A crystal of **4** suitable for X-ray diffraction was obtained by recrystallization from THF/pentane at $T = -30$ °C. The molecular structure of **4** is illustrated in Figure 1. The structural analysis confirms that **4** is the C(sp^2)−C(sp) cleavage product. Interestingly, the insertion of the metal center into the C−C bond of diphenylacetylene is selective, forming only one isomer with the alkynyl group trans to the phosphorus atom.

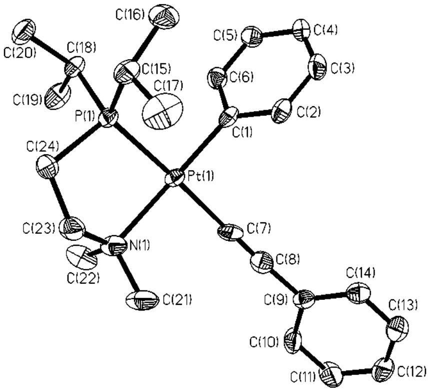
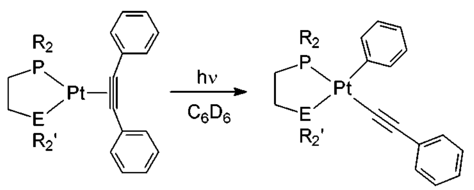


Figure 1. Molecular structure of (PN)PtPh(C≡CPh) (**4**) (ORTEP diagram; 30% probability ellipsoids).

The precursor (COD)Pt(PhC≡CPh) was also converted into symmetrically substituted Pt(0)−alkyne complexes bearing chelating P,P-ligands. Thus, the reaction of **1** with 1 equiv bis(diisopropylphosphino)ethane[8] (**5**) (dippe) or bis(dicyclohexylphosphino)ethane (**6**) (dcpe) led to the formation of the corresponding η^2-alkyne complexes (dippe)Pt(PhC≡CPh) (**7**) and (dcpe)Pt(PhC≡CPh)[9] (**8**) (eq 1). **7** and **8** were obtained as yellow, air- and moisture-sensitive solids in high yields after recrystallization from pentane/CH_2Cl_2. The $^{31}P\{^1H\}$ NMR spectra of **7** and **8** in C_6D_6 showed a singlet with Pt-satellites at δ = 77.1 ppm ($^1J_{Pt-P}$ = 3034 Hz) and δ = 68.2 ppm ($^1J_{Pt-P}$ = 3029 Hz), respectively. Analogous to compound **3**, migration of the metal center with subsequent insertion into the C−Ph bond was observed for compounds **7** and **8** upon irradiation with UV light. The C−C cleavage products (dippe)PtPh(C≡CPh) (**9**) and (dcpe)PtPh(C≡CPh) (**10**) were quantitatively generated after photolyzing solutions of **7** and **8** in C_6D_6 for 12 and 7 h, respectively (eq 2).



(2)

3, 7, 8

E = N, R = iPr, R'= Me: **4**
E = P, R = R'= iPr: **9**
E = P, R = R'= Cy: **10**

Colorless, air- and moisture-stable crystals of **9** and **10** were isolated after recrystallization. The $^{31}P\{^1H\}$ NMR spectra of the generated species each displayed two singlets with Pt-satellites

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[1] For recent reviews on C−C bond activation see: (a) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (b) Murakami, M.; Ito, Y. In *Topics in Organometallic Chemistry*; Murai, S., Ed.; Springer-Verlag: New York, 1999; Vol. 3, pp 96−129. (c) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119.

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[7] All photolysis experiments were conducted with an Oriel arc source using a 200-W Hg(Xe) bulb in Pyrex vessels or NMR tubes.

[8] (a) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185. (b) Burg, R. J.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203.

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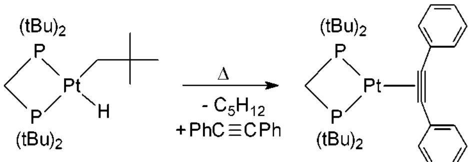
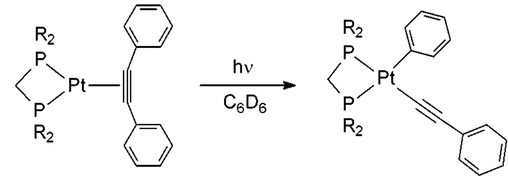
at $\delta = 63.3$ ppm ($^1J_{\mathrm{Pt-P}} = 2464$ Hz) and $\delta = 69.5$ ppm ($^1J_{\mathrm{Pt-P}} = 1575$ Hz) for **9** (C_6D_6) and two singlets with Pt-satellites at $\delta = 55.2$ ppm ($^1J_{\mathrm{Pt-P}} = 2461$ Hz) and $\delta = 61.9$ ppm ($^1J_{\mathrm{Pt-P}} = 1573$ Hz) for **10** (C_6D_6), indicating the formation of unsymmetrically substituted Pt-complexes.

We were also interested in photolysis experiments on Pt−diphenylacetylene complexes bearing highly constrained chelating P,P-ligands, as Hofmann has demonstrated high reactivity of such species.[10] The compound (dippm)Pt(PhC≡CPh) (**11**) was synthesized from **1** and dippm (**12**) (dippm = bis(diisopropylphosphino)methane[11]) according to eq 1. (dtbpm)Pt(PhC≡CPh) (**14**) (dtbpm = bis(di-*tert*-butylphosphino)methane[12]), however, was obtained from the corresponding Pt(II)neopentyl-hydride precursor **13**.[10] Reductive elimination at $T = 60$ °C in THF-d_8 in the presence of diphenylacetylene afforded the η^2-alkyne complex **14** (eq 3). **11** and **14** were obtained as orange solids after recrystallization from pentane or THF/hexanes.



13 **14** (3)

The smaller P−Pt−P angle in **11** and **14** compared to that in **3**, **7**, and **8** results in a significant change in the $^{31}P\{^1H\}$ chemical shifts; resonances at $\delta = 7.9$ ppm ($^1J_{\mathrm{Pt-P}} = 2513$ Hz) and $\delta = 26.6$ ppm ($^1J_{\mathrm{Pt-P}} = 2550$ Hz) were observed for **11** and **14**, respectively (C_6D_6). Solutions of (dippm)Pt(PhC≡CPh) and (dtbpm)Pt(PhC≡CPh) in C_6D_6 were irradiated with UV light and monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 20 h the conversion of **11** into the new product (**15**) was complete. **15** was obtained as colorless crystals after recrystallization from benzene/petroleum ether. The $^{31}P\{^1H\}$ spectrum of **15** showed two doublets ($^2J_{\mathrm{P-P}} = 32.4$ Hz) with Pt-satellites at $\delta = -23.1$ ppm ($^1J_{\mathrm{Pt-P}} = 2182$ Hz) and $\delta = -23.5$ ppm ($^1J_{\mathrm{Pt-P}} = 1226$ Hz). **14** was quantitatively converted into **16** after 16 h of irradiation. Colorless crystals of **16** were isolated after recrystallization from dichloromethane/diethyl ether. Two singlets with Pt-satellites at $\delta = -9.6$ ppm ($^1J_{\mathrm{Pt-P}} = 1228$ Hz) and -12.0 ppm ($^1J_{\mathrm{Pt-P}} = 2169$ Hz) were displayed in the $^{31}P\{^1H\}$ NMR spectrum. Once again the ^1H NMR spectrum of **15** and **16** showed ortho phenyl protons with the characteristic Pt-satellites. These results are consistent with the formation of unsymmetrically substituted Pt(II) complexes and phenyl groups σ-bonded to the metal center (eq 4).



(4)

R = iPr: **11**; R = tBu: **14** R = iPr: **15**; R = tBu: **16**

Furthermore, the C(sp^2)−C(sp) bond activation in **11** was confirmed by single-crystal X-ray diffraction. The molecular structure of **15** is shown in Figure 2.

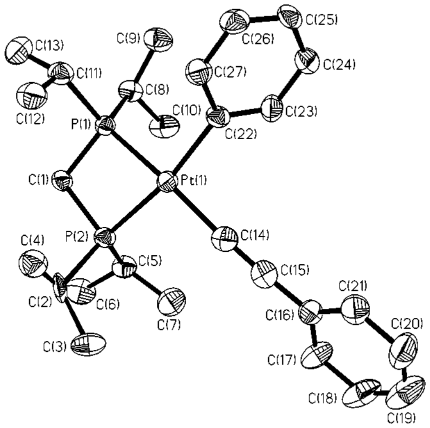
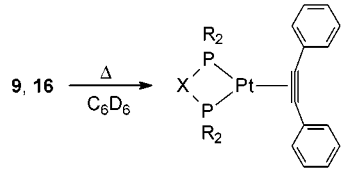


Figure 2. Molecular structure of (dippm)PtPh(C≡CPh) (**15**) (ORTEP diagram; 30% probability ellipsoids).

We have shown that the C−C bond activation in diphenylacetylene is a general feature in Pt−η^2-alkyne complexes, bearing chelating P,N- and P,P-ligands. However, alkyl groups attached to the donor atoms seem to be a prerequisite for the quantitative and selective formation of the C−C cleavage product. Anderson et al. reported on the photolysis of the Pt(II)−oxalate complex (dppe)Pt(C_2O_4) (dppe = bis(diphenylphosphino)ethane) in the presence of diphenylacetylene.[4] Upon extended photolysis the Pt−η^2-diphenylacetylene complex (dppe)Pt(PhC≡CPh)[13] (**17**) was obtained as the major product. The formation of (dppe)PtPh(C≡CPh) (**18**) was also detected. We independently synthesized **17** via the route shown in eq 1 and examined the photolysis experiment of the pure compound. After 24 h of irradiation 85% of the starting material was converted to approximately 40% of **18** and unidentified side-products.[14]

The oxidative addition of diphenylacetylene to the metal center turned out to be reversible. On thermal activation reductive elimination occurred, and the Pt−η^2-alkyne complexes were generated again. This reaction is shown for **9** and **16** in eq 5. *The thermal accessibility of this reverse reaction indicates that the oxidative addition of sp^2−sp C−C bonds in these systems is uphill thermodynamically.*



(5)

X = CH_2CH_2, R = iPr: **7**; X = CH_2, R = tBu: **14**

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Supporting Information Available: A listing of experimental procedures, data collection parameters, bond lengths, bond angles, fractional atomic coordinates, and anisotropic thermal parameters (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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