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Notes

Palladium(II) Complexes of α-Stabilized Phosphorus Ylides

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Summary: Using the α-stabilized phosphorus ylides $PhC(O)CH{=}PPh_2CH_2CH_2PPh_2{=}CHC(O)Ph$ *and* $Ph_3P{=}CHC(NMe_2){=}CH_2$*, novel palladium(II) complexes were synthesized:* $[PhC(O)CH{=}PPh_2CH_2CH_2PPh_2{=}CHC(O)Ph]PdCl_2$*, where two asymmetric carbon centers were formed, and the* η^3*-allyl complex* $[Ph_3P{=}CHC(NMe_2){=}CH_2]PdCl_2$ *are easily accessible by exchange of cycloocta-1,5-diene or benzonitrile in the corresponding palladium complexes. The molecular structures of both complexes were confirmed by X-ray crystal structure analysis.*

Introduction

The search for nonmetallocene catalysts in catalytic reactions, such as olefin polymerization, is the aim of extensive research activities.[1] Phosphorus ylide complexes have been well investigated.[2] They are versatile ligands for catalysts in a very small number of catalytic reactions such as, for example, the hydrogenation of olefins[3a] and the cyclotrimerization[3b] and polymerization of acetylenes,[3c] but the most important application is in the industrially used SHOP process.[3d] Thus, the nickel(II) complex $[Ph_2PCHC(Ph)O]NiPh(PPh_3)$, obtained by Keim et al. from the reaction of the α-carbonyl-stabilized ylide $Ph_3P{=}CHC(O)Ph$ with $Ni(COD)_2$ in the presence of PPh_3, is assumed to be one of the catalytically active species in this olefin oligomerization.[2b] α-Stabilized phosphorus ylides are distinguishable from nonstabilized ylides, since they can be easily handled due to an additional stabilization from delocalization of the negative charge. We recently reported the synthesis of $Ph_3P{=}CHC(NMe_2){=}CH_2$ by the reaction of $Ph_3P{=}CHC(O)Me$ with $Ti(NMe)_4$.[4] The bis-ylide $PhC(O)CH{=}PPh_2CH_2CH_2PPh_2{=}CHC(O)Ph$ was prepared by a synthetic route analogous to that for the already known ylides $Ph_3P{=}CHC(O)R$ (R = Ph, Me)[5] and $Ph_2PCH_2CH_2Ph_2P{=}CHC(O)Ph$.[6] Here we report the reactions of both ylides with Pd(II) complexes.

Results and Discussion

The diphosphine $Ph_2PCH_2CH_2PPh_2$ reacts with 2 equiv of phenacyl bromide, $BrCH_2C(O)Ph$, forming the corresponding phosphonium salt (Scheme 1). Further treatment with aqueous Na_2CO_3 solution leads to 2-fold elimination of HBr, giving the free ligand **1**.

The complexation of this ligand by palladium(II) is possible by exchange reactions of COD or benzonitrile starting from either $Cl_2Pd(COD)$ or $Cl_2Pd(PhCN)_2$. Such a substitution by the bis-ylide **1** is shown in Scheme 2. In the case of the reaction with $Cl_2Pd(COD)$ an addition of the ylide to the cycloocta-1,5-diene was not observed.[7]

The X-ray crystal structure analysis of **2** (Figure 1) confirmed that the bis-ylide bonds to the soft metal palladium in the C-coordination form, and therefore two stereogenic centers are formed. Only one of the possible diasteriomeric pairs, the one where both asymmetric carbon atoms adopt the same chirality, crystallizes as a racemic mixture (*R*,*R* and *S*,*S* enantiomers).

The coordination geometry is nearly square planar. As a result of steric interactions the coordination plane forms an angle with the remaining ligand fragment, such that there is no molecular symmetry.

A (η^3-allyl)palladium complex was obtained by exchange of COD or benzonitrile with $Ph_3P{=}CHC(NMe_2){=}CH_2$ in either $Cl_2Pd(COD)$ or $Cl_2Pd(PhCN)_2$ (Scheme 3).

The molecular structure of **3**, which was determined by X-ray crystallography, is depicted in Figure 2. In complex **3** an η^3-allyl ligand and two chloro atoms are coordinated to palladium(II). The atoms C1, C3, Cl1, and Cl2 form a distorted square around the metal with C2 above this plane.

The angle between the planes defined by Cl1, Pd, Cl2 and C1, C2, C3 is 118°, nearly the same as found in

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[1] Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem.* **1999**, *111*, 448; *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

[2] (a) Weber, L. In *The Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: 1982; Chapter 3. (b) Schmidbaur, H. *Angew. Chem.* **1983**, *95*, 980; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. (c) Navarro, R.; Urriolabeitia, E. P. *J. Chem. Soc., Dalton Trans.* **1999**, 4111. (d) Falvello, L. R.; Fernandez, S.; Navarro, R.; Urriolabeitia, E. P. *Inorg. Chem.* **2000**, *39*, 2957.

[3] (a) Grey, R. A.; Anderson, L. R. *Inorg. Chem.* **1977**, *16*, 3187. (b) Holy, N. L.; Baenziger, N. C.; Flynn, R. M. *Angew. Chem.* **1978**, *90*, 732. (c) Starzewski, K. A., O.; Witte, J. *Angew. Chem.* **1988**, *100*, 861; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 839. (d) Keim, W.; Bauer, R. S.; Chung, H. C.; Glockner, P. U.S. Patent 3635937, 1969. Keim, W.; Mason, R. F.; Glockner, P. U.S. Patent 3647914, 1972.

[4] Spannenberg, A.; Baumann, W.; Rosenthal, U. *Appl. Organomet. Chem.* **2000**, *14*, 611.

[5] Ramirez, F.; Dershowitz, S. *J. Org. Chem.* **1957**, *22*, 41.

[6] Oosawa, Y.; Miyamoto, T.; Saito, T.; Sasaki, Y. *Chem. Lett.* **1975**, 33.

[7] Vicente, J.; Chicote, M.-T.; MacBeath, C.; Fernandez-Baeza, J.; Bautista, D. *Organometallics* **1999**, *18*, 2677.

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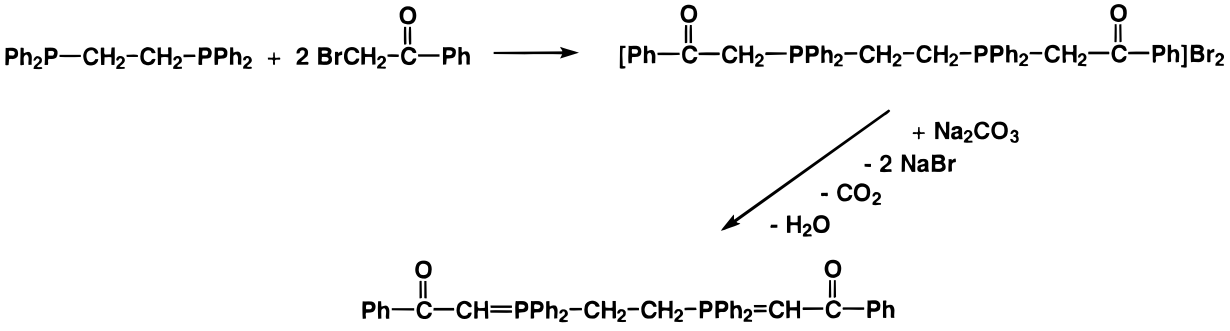
Scheme 1



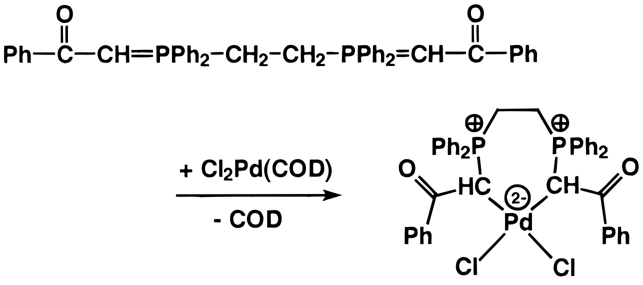
1

other η^3-allyl complexes.[8,9] The distance P–C1 is comparable with those in other η^3-phosphonium allyl-ylide complexes.

The NMR spectra of both complexes (**2** and **3**) exhibit features characteristic of a C-coordination of the ylides.[10] The phosphorus resonance suffers a positive coordination shift of 8.1 ppm (**2**) or 12.1 and 16.1 ppm (**3**), whereas negative (high-field) shifts would be expected for an O-coordination. The decrease of the coupling constants observed at the methine group of complex **3** ($^2J_{P,H}$ by 14.5 Hz, $^1J_{P,C}$ by 56 Hz) is also indicative of this bonding mode.

A special feature of the α-vinyl substituted ylide $Ph_3P{=}CHC(NMe_2){=}CH_2$ in complex **3** is that the olefinic double bond participates in the coordination. Therefore, and in agreement with the crystal structure of **3**, a high-field shift for the olefinic protons and a large geminal coupling constant of 5.5 Hz were observed. An allylic (η^3) bonding mode results in a substitution pattern (Ph_3P group in the *E* position) which was confirmed by ^1H NOE measurements.

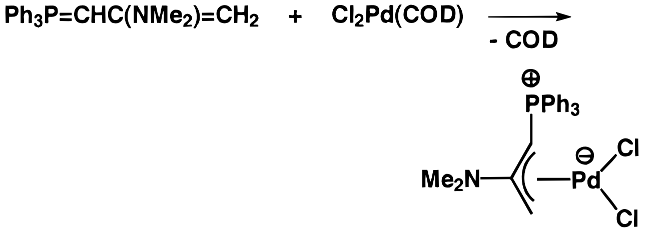
Scheme 2



2

The coordination of the bis-ylide **1** to $PdCl_2$ creates two stereogenic centers of the same configuration, and complex **2** exhibits C_1 symmetry, as indicated by the presence of two ^{31}P NMR signals (doublets of 4 Hz at 29.8 and 33.1 ppm). All atoms of the ligand are nonequivalent and discriminable (although no attempt was made to identify all resonances of the phosphorus bound phenyl groups) and were assigned with the aid of a ^1H NOESY spectrum. Interestingly, under the measuring conditions ($T = 297$ K, mixing time 1.5 s) not only NOE correlations are detected but also cross-peaks of opposite phase between 1-H and 9-H, between the *ortho* protons of the benzoyl group at C1 and of the benzoyl group at C9, between the respective *meta* and *para* protons, and also between the *ortho* protons of phenyl 19 and of phenyl 31 (see Figure 1 for atom numbering). A kind of chemical exchange must be operative, and inspection of a ball-and-stick model revealed that the required positional changes are easily achieved if the configuration of both stereogenic centers, C1 and C9, which is *S* for the depicted molecules, is inverted, perhaps after ligand dissociation. Complex **2** must therefore be regarded as stereochemically labile.

Scheme 3



3

The complexes **2** and **3** are moderately sensitive to air and moisture. Both are very soluble in halogenated solvents as dichloromethane and insoluble in nonpolar solvents such as *n*-hexane.

Experimental Section

The bis-ylide **1** was prepared by a synthetic route analogous to that for already known ylides.[5,6] The synthesis of the ylide $Ph_3P{=}CHC(NMe_2){=}CH_2$ was described previously.[4] All other reagents were obtained commercially and used as supplied. The operations were carried out under an inert atmosphere (argon) using Schlenk techniques. Prior to use, solvents were dried and freshly distilled under argon. NMR spectra were recorded on a Bruker ARX 400 spectrometer. ^1H and ^{13}C chemical shifts are referenced to the solvent resonances and reported relative to tetramethylsilane. Melting points were determined in sealed capillaries on a Büchi 535 apparatus. Elemental analyses were performed with a Leco CHNS-932 elemental analyzer. The IR spectra were recorded on a Nicolet

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(8) Facchin, G.; Bertani, R.; Calligaris, M.; Nardin, G.; Mari, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1381 and references therein.

(9) Werner, H.; Mahr, N.; Frenking, G.; Jonas, V. *Organometallics* **1995**, *14*, 619.

(10) Albanese, J. A.; Staley, D. L.; Rheingold, A. L.; Burmeister, J. L. *Inorg. Chem.* **1990**, *29*, 2209 and references therein.

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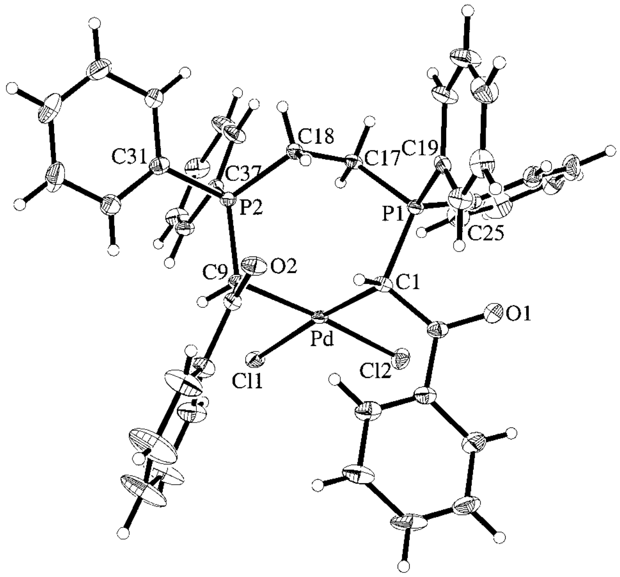

Figure 1. Crystal structure of **2**. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): C1−P1 = 1.816(6), C9−P2 = 1.787(6), Pd−Cl1 = 2.380(2), Pd−Cl2 = 2.337(2); Cl1−Pd−Cl2 = 88.82(6), C1−Pd−C9 = 94.9(2).

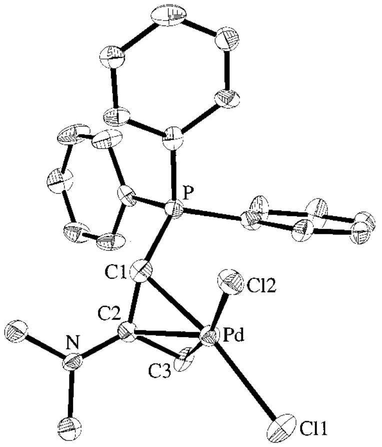

Figure 2. Crystal structure of **3**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Pd−Cl1 = 2.359(3), Pd−Cl2 = 2.389(3), Pd−C1 = 2.108(12), Pd−C2 = 2.231(12), Pd−C3 = 2.090(12), C1−P = 1.77(1), C1−C2 = 1.46(2), C2−C3 = 1.44(2); Cl1−Pd−Cl2 = 97.0(1).

Magna 550 spectrometer. X-ray data of compound **2** and **3**[11] were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86)[12] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[13] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

$PhC(O)CH{=}PPh_2CH_2CH_2PPh_2{=}CHC(O)Ph$ (1). Mp: 236 °C. Anal. Calcd for $C_{42}H_{36}O_2P_2\cdot{}^1/_3CH_2Cl_2$ (634.69): C, 76.69; H, 5.57. Found: C, 76.84; H, 5.62. ^1H NMR (CD_2Cl_2; δ, ppm): 3.24 ("d", 4H, P−CH_2), 4.24 ("t", 2H, P═CH), 7.40 (m, 6H, C−Ph), 7.46 (8H, P−Ph *m*), 7.54 (4H, P−Ph *p*), 7.78 (8H, P−Ph *o*), 7.98 (m, 4H, C−Ph). ^{13}C NMR (CD_2Cl_2; δ, ppm): 18.9 ("t", P−CH_2), 47.1 ("t", P═CH), 127.1 (Ph), 127.9 (*i*-C(O)Ph), 128.1 (Ph), 129.5 ("t", *o*/*m*-P−Ph), 129.7 (*p*-C−Ph), 132.0 ("t", *o*/*m*-P−Ph), 132.5 (Ph), 141.5 ("t", *i*-P−Ph), 185.5 (CO). ^{31}P NMR (CD_2Cl_2; δ, ppm): 17.7. IR (KBr; $\tilde{\nu}_{CO}$, cm^{-1}): 1509.

$[PhC(O)CH{=}PPh_2CH_2CH_2PPh_2{=}CHC(O)Ph]PdCl_2$ (2). $Cl_2Pd(PhCN)_2$ (225 mg, 0.59 mmol) in 20 mL of CH_2Cl_2 was added to $PhC(O)CH{=}PPh_2CH_2CH_2PPh_2{=}CHC(O)Ph$ (373 mg, 0.59 mmol) in 20 mL of CH_2Cl_2. After it was stirred for 1 h, the solution was filtered, concentrated in vacuo, and layered with *n*-hexane. At −30 °C a yellow solid (220 mg, 46%) precipitated.

Mp: 225 °C dec. Anal. Calcd for $C_{42}H_{36}Cl_2O_2P_2Pd\cdot CH_2Cl_2$ (812.02): C, 57.58; H, 4.27. Found: C, 57.77; H, 4.51. ^1H NMR (CD_2Cl_2; δ, ppm): 2.90 (m, 2H, CH_2), 3.11 (m, 1H, CH_2), 3.44 (m, 1H, CH_2), 4.42 (d, $^2J_{H,P} = 2.9$ Hz, 1-H), 5.95 (d, $^2J_{H,P} = 1.1$ Hz, 9-H), 7.91/6.66/7.14 (*o*/*m*/*p*, 1-benzoyl), 8.54/7.52/7.63 (*o*/*m*/*p*, 9-benzoyl), 7.50/7.65/8.29/8.48 (2H each, *o*-P−Ph). ^{13}C NMR (CD_2Cl_2; δ, ppm ($J_{C,P}$)): 16.7 (62 Hz, CH_2), 20.1 (63 Hz, CH_2), 21.0 (48 Hz, $^1J_{C,H} = 143$ Hz, C9), 27.6 (43 Hz, $^1J_{C,H} = 133$ Hz, C1), 129.1/127.7/131.8 (*o*/*m*/*p*, 1-benzoyl), 129.9, 133.5, 133.4 (*o*/*m*/*p*, 9-benzoyl), 131.9 (9 Hz)/133.0 (9 Hz)/134.5 (10 Hz)/136.6 (10 Hz) (*o*-P−Ph), 128.5 (13 Hz)/129.8 (12 Hz)/129.9 (12 Hz)/130.1 (12 Hz) (*m*-P−Ph), 200.1/202.1 (CO). ^{31}P NMR (CD_2Cl_2; δ, ppm): 29.8 (d, $^2J_{P,P} = 4$ Hz, P1), 33.1 (d, $^2J_{P,P} = 4$ Hz, P2). IR (KBr; $\tilde{\nu}_{CO}$, cm^{-1}): 1679, 1632.

$[Ph_3P{=}CHC(NMe_2){=}CH_2]PdCl_2$ (3). $Cl_2Pd(PhCN)_2$ (302 mg, 0.79 mmol) in 20 mL of CH_2Cl_2 was added to $Ph_3P{=}CHC(NMe_2){=}CH_2$ (272 mg, 0.79 mmol) in 20 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h and then filtered. The filtrate was concentrated in vacuo and layered with *n*-hexane. At −30 °C a yellow solid (144 mg, 35%) precipitated. Mp: 214 °C. Anal. Calcd for $C_{23}H_{24}Cl_2NPPd$ (522.75): C, 52.85; H, 4.63; N, 2.68. Found: C, 52.46; H, 4.36; N, 2.51. ^1H NMR (CD_2Cl_2; δ, ppm): 1.54 (d, $^2J_{H,H} = 5.5$ Hz, $CH_2(E)$), 2.98 (s, NMe_2), 3.08 (dd, $^2J_{H,H} = 5.5$ Hz, $^4J_{H,H} = 2.9$ Hz, $CH_2(Z)$), 3.98 (dd, $^4J_{H,H} = 2.9$ Hz, $^2J_{H,P} = 3.6$ Hz), 7.67 (m, *m*-CH), 7.80 (m, *p*-CH), 7.87 (m, *o*-CH). ^{13}C NMR (CD_2Cl_2; δ, ppm): 28.0 ($^1J_{C,P} = 76$ Hz, $^1J_{C,H} = 151$ Hz, CH), 38.3 ($^1J_{C,H} = 161$ Hz, CH_2), 40.3 ($^1J_{C,H} = 138$ Hz, NMe_2), 121.8 ($^1J_{C,P} = 89$ Hz, *i*-C), 130.1 ($^3J_{C,P} = 13$ Hz, *m*-CH), 134.5 ($^2J_{C,P} = 10$ Hz, *o*-CH), 134.9 ($^4J_{C,P} = 3$ Hz, *p*-CH), 144.7 ($^2J_{C,P} = 7$ Hz, C_{quat}). ^{31}P NMR (CD_2Cl_2; δ, ppm): 18.6. IR (Nujol; $\tilde{\nu}_{CCC}$, cm^{-1}): 1541.

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Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) For the X-ray crystal structure analysis suitable crystals of **2** and **3** were obtained from a CH_2Cl_2/hexane solution. The crystals of both complexes contain CH_2Cl_2 as solvent. Crystal data for **2**: crystal dimensions 0.4 × 0.3 × 0.3 mm, yellow prisms, space group $P2_1/n$, monoclinic, $a = 11.832(2)$ Å, $b = 16.017(3)$ Å, $c = 25.262(5)$ Å, $\beta = 96.11(3)°$, $V = 4760(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.488$ g cm^{-3}, 12 728 reflections measured, 7000 were independent of symmetry and 4594 were observed ($I > 2\sigma(I)$), R1 = 0.056, wR2(all data) = 0.149, 505 parameters. Crystal data for **3**: crystal dimensions 0.2 × 0.1 × 0.1, yellow prisms, space group $P\bar{1}$, triclinic, $a = 8.395(2)$ Å, $b = 12.482(2)$ Å, $c = 13.202(3)$ Å, $\alpha = 99.94(3)°$, $\beta = 91.40(3)°$, $\gamma = 94.95(3)°$, $V = 1356.5(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.592$ g cm^{-3}, 2782 reflections measured, 2782 were independent of symmetry, and 1777 were observed ($I > 2\sigma(I)$), R1 = 0.070, wR2(all data) = 0.182, 281 parameters.

(12) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(13) Sheldrick, G. M. SHELXL-93; University of Göttingen, Göttingen, Germany, 1993.