Phosphanorbornadienephosphonates as a New Type of Water-Soluble Phosphines for Biphasic Catalysis

Stéphane Lelièvre, François Mercier, and François Mathey*

Laboratoire "Hétéroéléments et Coordination" URA CNRS 1499, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

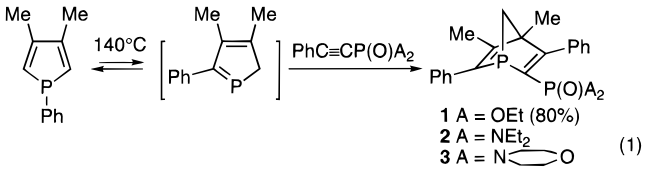
Received December 6, 1995[⊗]

The reaction of (phenylethynyl)phosphonates or- phosphonamides with 1-phenyl-3,4-dimethylphosphole at 140 °C affords the corresponding α-P(O)-substituted 1-phosphanorbornadienes (**1**−**3**). The corresponding PO_3Na_2 salt (**5**) displays some solubility in water (20 g/L) but is a poor ligand both for the rhodium-catalyzed hydrogenation and hydroformylation of olefinic bonds. The reaction of an unsubstituted ethynylphosphonamide with the same phosphole yields a 3:1 mixture of α- and *β*-P(O)-substituted 1-phosphanorbornadienes **7** and **8**. The *β*-PO_3Na_2 salt (**10**) is a good ligand for the hydrogenation of (*Z*)-α-(*N*-acetamido)cinnamic acid and displays a high solubility in water (230 g/L). The chelation of rhodium by the α-P(O)-substituted 1-phosphanorbornadienes probably explains the loss of hydrogenation efficiency for $[RhL_2]^+$ when L = **5**.

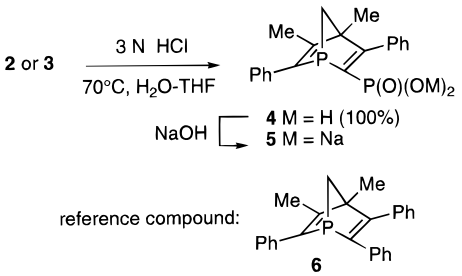
1-Phosphanorbornadienes have shown excellent qualities as ligands in the rhodium-catalyzed hydrogenation[1] and hydroformylation[2] of alkenes. In view of the growing academic and industrial interest in biphasic catalysis,[3] water-soluble versions of these phosphanorbornadienes represent a logical further development. In line with this, the *para*-sulfonation of the phenyl substituents of 2,3,6-triphenyl-4,5-dimethyl-1-phosphanorbornadiene has produced the so-called NORBOS which shows an outstanding activity in the biphasic hydroformylation of propene.[4] We have decided to investigate another possible route to such species which involves the introduction of the water-solubilizing functionality during the construction of the bicyclic system. For synthetic convenience, we have selected the phosphonate functionality which has recently been introduced[5,6] as a promising alternative to the ubiquitous sulfonate group.

Results and Discussion

Since the synthesis of 1-phosphanorbornadienes involves the [4 + 2] cycloaddition of a transient 2*H*-phosphole with an alkyne,[7,8] we first decided to study the reaction of various (phenylethynyl)phosphonic acid derivatives with the transient 2-phenyl-3,4-dimethyl-5*H*-phosphole as produced by thermal isomerization of 1-phenyl-3,4-dimethylphosphole (eq 1). The reaction almost exclusively produces the phosphanorbornadiene having the phosphoryl group located on C_2. This regioselectivity is demonstrated by the ^{31}P NMR spectra which display AX systems with *J*(A−X) values in the range of 58−67 Hz, *i.e.*, strictly incompatible with three-bond couplings, see later. Furthermore, the ^{13}C spectra show characteristic resonances for the C_2 carbons as doublets of doublets, *e.g.*, for **3**, *δ* C_2 143.19, $^1J(C-P)$ = 155 and 45.5 Hz ($CDCl_3$). The acid hydrolysis of **2** or **3** quantitatively produces the expected phosphonic acid **4** whose sodium salt **5** is moderately water-soluble (20 g/L) (eq 2). In spite of this rather poor solubility, we noticed that **5** is quantitatively extracted by water from a saturated toluene solution (solubility *ca.* 10 g/L at 50 °C). Thus, **5** was potentially of some interest as a substitute to the sodium salt of triphenylphosphinemonosulfonic acid which forms the basis of the new oxo process developed by Union Carbide for the hydroformylation of higher olefins.[9] Consequently, we performed some preliminary experiments in order to check the catalytic activity of $[RhL_2]^+$ (L = **1**−**3**, **5**) in the hydrogenation of (*Z*)-α-(*N*-acetamido)cinnamic acid or 1-methylcyclohexene (rt, $p(H_2)$ = 3 bar, catalyst: substrate = 1:100, THF for **1**−**3**, water/toluene (1/1) or MeOH/H_2O (1/4) for **5**). In all cases, the results were poor or extremely poor, in contrast to the high activity observed for the nonfunctional 1-phosphanorbornadiene **6**.[1] Poor results were also observed in the hydroformylation of 1-hexene as catalyzed by the $[Rh(CO)_2Cl]_2$ + 2L (L = **5**) systems. Since



(1)



(2)

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

(1) Mathey, F.; Neibecker, D.; Brèque, A. (SNPE), Fr. Pat. 25 88 197, Oct 3, 1985; *Chem. Abstr.* **1987**, *107*, 219468v.

(2) Neibecker, D.; Reau, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 500.

(3) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524.

(4) Herrmann, W. A.; Kohlpaintner, C. W.; Manatsberger, R. B.; Bahrmann, H.; Kottmann, H. *J. Mol. Catal. A* **1995**, *97*, 65.

(5) Ganguly, S.; Mague, J. T.; Roundhill, D. M. *Inorg. Chem.* **1992**, *31*, 3500.

(6) Schull, T. L.; Fettinger, J. C.; Knight, D. A. *J. Chem. Soc., Chem. Commun.* **1995**, 1487.

(7) Mathey, F.; Mercier, F.; Charrier, C.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1981**, *103*, 4595.

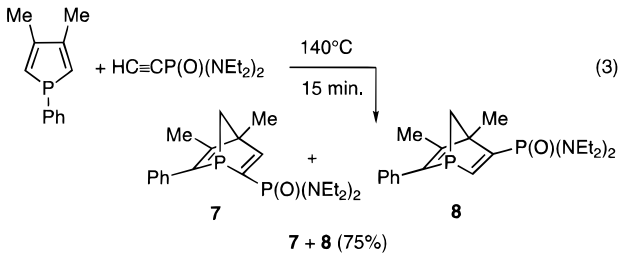
(8) Laporte, F.; Mercier, F.; Ricard, L.; Mathey, F. *Bull. Soc. Chim. Fr.* **1993**, *130*, 843.

(9) Haggin, J. *Chem. Eng. News* **1995**, April 17, 25.

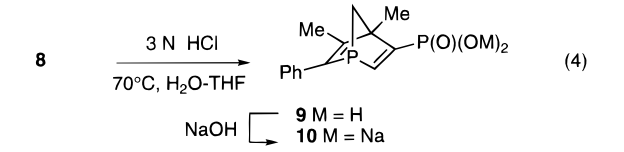
S0022-3263(95)02171-2 CCC: $12.00

we suspected that the catalytic cycles were blocked by the formation of P,P(O)-chelates, we investigated more precisely the reaction of **3** with $[Rh(COD)_2]^+PF_6^-$. In **3**, the ^{31}P parameters are δ(P) −6, δ(P═O)+22, J(P−P) = 58 Hz ($CDCl_3$). The IR (P═O) stretching vibration occurs at 1198 cm^{-1} (CH_2Cl_2). In the 1:1 rhodium complex, both ^{31}P resonances are significantly shifted downfield and P···Rh couplings appear: δ(P) +35.5, δ(P═O) +38.5, J(P−P) = 82.8 Hz, ^1J(P−Rh) = 155.7 Hz, ^2J(P−O−Rh) = 7.8 Hz. The IR (P═O) band also shifts to lower frequency but is difficult to assign. These results fit quite well the literature data on P,P(O)-chelates of Rh(I).[10] For an Rh:L ratio of 1:2, similar observations are made but the precise data are more difficult to collect due to the formation of diastereomeric complexes.

The detrimental effect of the α-P(O) groups on the catalytic activity led us to investigate the synthesis of the β-substituted phosphonate derivatives of 1-phosphanorbornadienes. The reaction of an unsubstituted ethynyl-phosphonamide with the same transient 2*H*-phosphole as used previously yields a mixture of the two possible regioisomers with a α/β ratio of 3:1 (eq 3). The



two regioisomers are easily separated by chromatography on silica gel. The ^{31}P spectrum of **7** displays a characteristic AX spectrum, δ_A −4.6, δ_X +26.0, J(A−X) = 49 Hz, indicative of an α-substitution whereas **8** displays two singlets at −22.1 and + 26.1 ($CDCl_3$). The hydrolysis of **8** leads to the corresponding acid **9** whose sodium salt **10** is highly soluble in water (230 g/L) (eq 4). Using



ligand **10** under the same conditions as those previously described for **5**, (Z)-α-(*N*-acetamido)cinnamic acid is quantitatively hydrogenated in 1 h at rt (note that no hydrogenation is observed with **5**). Our hypothesis on the freezing of the catalytic cycle due to the chelation of rhodium by the α-P(O) group of **5** is thus fully confirmed. The improvement is less impressive in the hydroformylation of 1-hexene as catalyzed by the $[Rh(CO)_2Cl]_2$ + 2L (L = **10**) system. Using the following conditions, 80 °C, $p(H_2)$ = 10 bar, p(CO) = 10 bar, catalyst:substrate = 1:100, water/toluene (1/1), we found that **10** is indeed better than **5**. Total yield of aldehydes: 89% (**10**) vs 66% (**5**). The normal/iso ratio is almost the same 0.88 (**10**) vs 1 (**5**). In that case, the potential P(O)-chelation seems to have a less significant effect on the catalytic cycle. This may be due to the higher temperature used for the hydroformylation experiments.

(10) Wegman, R. W.; Abatjoglou, A. G.; Harrison, A. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1891.

Experimental Section

General experimental information is identical to that previously reported.[11] Phenylacetylene, (trimethylsilyl)acetylene, (Z)-α-(*N*-acetamido)cinnamic acid, 1-hexene, and 1-methylcyclohexene were purchased from Aldrich. The 1-phenyl-3,4-dimethylphosphole,[12] $(Et_2N)_2P(O)Cl$,[13] $[O(CH_2CH_2)_2N]_2$ P(O)-Cl,[14] diethyl (phenylethynyl)phosphonate,[15] *N,N,N,N*-tetraethylethynylphosphinamine[16] $[Rh(COD)_2]^+$ PF_6^-,[17] and $[Rh(CO)_2Cl]_2$[18] were prepared according to literature procedures.

Diethyl (4,5-Dimethyl-3,6-diphenyl-1-phosphanorbornadien-2-yl)phosphonate (1). A mixture of (phenylethynyl)-phosphonate (2.5 g, 10.6 mmol) and phosphole (2.0 g, 10.6 mmol) was heated at 150 °C for 3 h in a sealed tube. The oily product was chromatographed with 50/50 CH_2Cl_2/AcOEt as eluent to yield a yellow oil (90% yield): ^{31}P NMR ($CDCl_3$) δ 18.0 (d, J = 67.4 Hz), −7.6 (d, J = 67.4 Hz); ^1H NMR ($CDCl_3$) δ 0.98 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H), 1.32 (d, J = 1.2 Hz, 3H), 2.08 (s, 3H), 2.15 (m, 2H), 3.70 (m, 2H), 3.9 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 66.0, 73.5 (dd, J = 6.0 Hz and 18.0 Hz), 140.5 (dd, J = 41.6 Hz and 196.0 Hz), 182.48 (d, J = 9.7 Hz); mass spectrum m/z 426 (M^+, 7), 239 (M − $C_{12}H_{12}P$, 100).

***N,N,N,N*-Tetraethyl(4,5-dimethyl-3,6-diphenyl-1-phosphanorbornadien-2-yl)phosphonamide (2).** A mixture of alkynylphosphonamide (7.7 g, 0.03 mmol) and phosphole (5.6 g, 0.03 mmol) was heated at 140 °C for 15 min in a sealed tube. Flash chromatography using 50/50 EtOAc/CH_2Cl_2 as eluent gave 10.6 g of a yellow oil (80% yield): ^{31}P NMR ($CDCl_3$) δ −6.5 (d, J = 42 Hz), 25.5 (d, J = 42 Hz); ^1H NMR ($CDCl_3$) δ 0.7 (t, J = 7.2 Hz, 4H), 1.2 (s, 3H), 2.0 (m, 2H), 2.1 (s, 3H), 2.6 (m, 6H), 2.9 (m, 6H). ^{13}C NMR ($CDCl_3$) δ 66.4, 74.5 (dd, J = 4.6 Hz and 13.7 Hz), 146.0 (dd, J = 44.3 Hz and 152.6 Hz), 179.8 (d, J = 8.5 Hz); mass spectrum m/z (relative intensity) 480 (M^+, 6), 293 (M − $C_{12}H_{12}P$, 100).

(4,5-Dimethyl-3,6-diphenyl-1-phosphanorbornadien-2-yl)phosphonamide (3). The product was prepared by the same procedure as for **2**. **3**: white solid recrystallized in 80/20 hexane/toluene (85% yield, mp 163 °C); ^{31}P NMR ($CDCl_3$) δ −6 (d, J = 58 Hz), 22 (d, J = 58 Hz); ^1H NMR ($CDCl_3$) δ 1.27 (s, 3H), 2.10 (s, 3H), 2.15 (m, 2H), 2.66 (m, 4H), 2.93 (m, 4H), 3.21 (m, 4H), 3.49 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 66.8 (dd, J = 6.3 Hz and J = 19.5 Hz), 74.3 (dd, J = 5.5 Hz and J = 15.0 Hz), 143.2 (dd, J = 45.5 Hz and 154.9 Hz), 183.1 (d, J = 9.3 Hz); mass spectrum m/z (relative intensity) 508 (M^+, 3), 321 (M^+ − $C_{12}H_{12}P$, 100). Anal. Calcd for $C_{28}H_{34}O_3N_2P_2$: C, 66.1; H, 6.73; N, 5.50; P, 12.18. Found: C, 65.97; H, 6.78; N, 5.28; P, 11.59.

(4,5-Dimethyl-3,6-diphenyl-1-phosphanorbornadien-2-yl)phosphonic Acid (4). A mixture of **2** (2.5 g, 5.6 mmol) and 3 N HCl (1 mL) in THF (15 mL) was heated at 70 °C for 18 h. The solution was concentrated, and the product was extracted with CH_2Cl_2. It was recrystallized from 80/20 hexane/toluene to give a white solid (90% yield, mp 150 °C); ^{31}P NMR ($CDCl_3$) δ −10.5 (d, J = 73.0 Hz), 18.4 (d, J = 73.0 Hz); ^1H NMR ($CDCl_3$) δ 1.25 (3H), 2.0 (3H), 2.06 (m, 2H); ^{13}C NMR (acetone-d_6) δ 67.5, 75.0 (dd, J = 5.5 Hz and J = 16.8 Hz), 143.0 (dd, J = 41.4 Hz and J = 196.1 Hz), 180.6 (d, J = 10.2 Hz). Anal. Calcd for $C_{20}H_{20}O_3P_2$: C, 64.86; H, 5.44; P, 16.72. Found: C, 64.60; H, 5.49; P, 16.55.

Disodium (4,5-Dimethyl-3,6-diphenyl-1-phosphanorbornadien-2-yl)phosphonate (5). A solution of NaOH (0.5 N, 20 mL) was added to a solution of phosphonic acid **4** (1.85 g, 5 mmol) in CH_2Cl_2 (10 mL) and shaked for 5 min. After decantation the water layer was separated and concentrated. A white solvated solid crystallized. **5**: ^{31}P NMR (D_2O) δ −8.8 (d, J = 34 Hz), 8.7 (d, J = 34 Hz); ^1H NMR (D_2O) δ 0.92 (3H),

(11) Laporte, F.; Mercier, F.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1994**, *116*, 3306.
(12) Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.
(13) Cowley, A. H.; Pinnell, R. P. *J. Am. Chem. Soc.* **1965**, *87*, 4454.
(14) Ning, R. Y.; Fryer, R. I.; Madan, P. B.; Sluboski, B. C. *J. Org. Chem.* **1976**, *41*, 2720.
(15) Chatta, M. S.; Aguiar, A. M. *J. Org. Chem.* **1971**, *36*, 2719.
(16) Fluck, E.; Kuhm, P. *Phosphorus Sulfur Silicon* **1989**, *42*, 123.
(17) Schrock, R. R.; Osborn, J. *J. Am. Chem. Soc.* **1971**, *93*, 3089.
(18) Mc Cleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

1.7 (3H), 1.9 (m, 2H); ^{13}C NMR (D_2O) δ 67.1, 72.8 (dd, J = 4.4 Hz and J = 14.0 Hz), 149.1 (dd, J = 37.8 Hz and J = 170.8 Hz). Anal. Calcd for $C_{20}H_{18}Na_2P_2O_3 \cdot 7\ H_2O$: C, 44.48; H, 5.92; P, 11.48. Found: C, 44.25; H, 5.51; P, 11.81.

***N,N,N,N*-Tetraethyl(4,5-dimethyl-6-phenyl-1-phosphanorbornadien-2-yl (and 3-yl))phosphonamide (7 and 8).** A mixture of ethynylphosphonamide (3.0 g, 14 mmol) and phosphole (2.6 g, 14 mmol) was heated at 140 °C for 15 min. The brown oil was chromatographed with 1/1 toluene/AcOEt as eluent to give **8** as an oil (1.1 g, 18% yield). **8**: ^{31}P NMR ($CDCl_3$) δ −22.1 and 26.1; ^{1}H NMR ($CDCl_3$) δ 1.0 (t, J = 7.2 Hz, 6H), 1.12 (t, J = 7.2 Hz, 6H), 1.81 (s, 3H), 2.0 (m, 2H), 2.08 (s, 3H), 2.92 (m, 4H), 3.10 (m, 4H), 7.60 (dd, J = 12.8 Hz and J = 44.3 Hz); ^{13}C NMR ($CDCl_3$) δ 67.3 (d, J = 8.2 Hz), 71.7 (dd, J = 4.8 Hz and J = 16.0 Hz), 158.0 (dd, J = 4.6 and J = 36.4 Hz), 162.1 (dd, J = 4.6 Hz and J = 146.6 Hz); mass spectrum m/z (relative intensity) 404 (M^+, 45), 286 ($M^+ - C_4H_{20}ONP$, 100). Anal. Calcd for $C_{22}H_{34}ON_2P_2$: C, 65.32; H, 8.47; N, 6.92; P, 15.31. Found: C, 65.11; H, 8.18; N, 6.78; P, 14.93.

Then with EtOAc as eluent **7** was obtained as an oil (3.3 g, 54% yield): ^{31}P NMR ($CDCl_3$) δ −4.6 (d, J = 49.2 Hz), 26.0 (d, J = 49.2 Hz); ^{1}H NMR ($CDCl_3$) δ 0.78 (t, J = 7.0 Hz, 6H), 1.07 (t, J = 7.0 Hz, 6H), 1.61 (s, 3H), 1.98 (m, 5H), 2.73 (m, 4H), 3.13 (m, 4H), 7.99 (dd, J = 6.5 Hz and J = 12.5 Hz); ^{13}C NMR ($CDCl_3$) δ 67.3, 68.9 (dd, J = 5.0 Hz and J = 14.1 Hz), 151.6 (dd, J = 47.2 Hz and J = 149.4 Hz), 171.5 (d, J = 7.3 Hz); mass spectrum m/z (relative intensity): 404 (M^+, 16), 191 ($M^+ - C_{14}H_{14}P$, 100).

(4,5-Dimethyl-6-phenyl-1-phosphanorbornadien-3-yl)-phosphonic Acid (9). This compound was obtained as an oil by following the same procedure as for **4**. **9**: ^{31}P NMR ($CDCl_3$) δ −20.0, 17.5; ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 3H), 1.96 (m, 5H), 8.0 (dd, J = 14.8 Hz and J = 43.9 Hz); ^{13}C NMR ($CDCl_3$) δ 68.3, 70.7 (dd, J = 5.7 Hz and J = 18.5 Hz), 158.2 (d, J = 185 Hz), 160.9 (dd, J = 6.3 Hz and J = 37.0 Hz).

Disodium (4,5-Dimethyl-6-phenyl-1-phosphanorbornadien-3-yl)phosphonate (10). This salt was obtained as a solvate (see 5). ^{31}P NMR (D_2O) δ −24.0 and 7.6; ^{1}H NMR (D_2O) δ 1.6 (3H), 1.8 (m, 2H), 1.9 (3H); ^{13}C NMR (D_2O) δ 70.9, 72.9 (dd, J = 5.0 Hz and 15.0 Hz), 150.2 (dd, J = 7.2 Hz and J = 27.7 Hz), 171.1 (d, J = 163.5 Hz).

Supporting Information Available: Additional preparations and copies of NMR spectra (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9521716