Inorg. Chem. **1994,** *33,* 175–177 **175**

Notes

Nucleophilic Addition of a Water-Soluble Phosphine to Aldehydes. Isolation of (1-Hydroxyalkyl)phosphonium Salts and the Crystal Structure of the (1-Methoxy-1-benzyl)(*m*-sulfonatophenyl)diphenylphosphonium Salt

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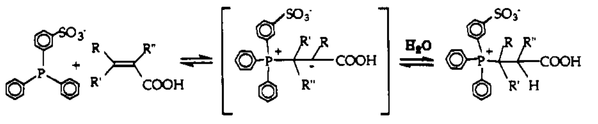
Received July 20, 1993

Introduction

Water soluble organometallic chemistry has received significant interest in the last few years, particularly in the area of biphasic catalysis. The most widely studied water soluble transition metal complexes are those with sulfonated phosphines, e.g. (*m*-sulfonatophenyl)diphenyl phosphine (TPPMS) and tris(*m*-sulfonatophenyl)phosphine (TPPTS).[2a–c] Sulfonated tertiary phosphines are employed, for example, in a low temperature and pressure industrial hydroformylation process[2d–f] and in laboratory scale asymmetric hydrogenations.[3] These complexes display spectroscopic properties similar to their water-insoluble analogues.[4] Consequently, they are often assumed to have the same catalytic properties and utilize a similar mechanism. However, water often plays an intimate role in aqueous catalysis in unanticipated ways, and many factors need to be taken into account that are irrelevant in organic solvents.[5]

Phosphonium salts are known to be formed in the reaction of tertiary phosphines with activated olefins, acetylenes, and aldehydes.[6] For example, Larpent and Patin have prepared a series of new compounds by reacting TPPMS and TPPTS with various unsaturated carboxylic acids in aqueous solution (eq 1).[7] The



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driving force for this reaction is the protonation of the carbanionic intermediate, **1**, by water, hence displacing the equilibrium to the right. Under typical catalytic hydrogenation conditions in organic solvents with $Rh(PPh_3)_3Cl$, this equilibrium is shifted far to the left and this reaction does not have important implications for the process. However, this is not the case for aqueous hydrogenations utilizing the related catalyst, $Rh(TPPMS)_3Cl$, where we have observed that the reaction between the activated olefins and TPPMS provides phosphonium salts.[8a] Indeed in some instances, this reaction serves to enhance the catalytic activity by consuming free phosphine ligand.[8b] Examples of formation of (1-hydroxyalkyl)phosphonium salts are considerably rarer. Such compounds have been synthesized from the nucleophilic addition of a (usually aliphatic) phosphine to the carbonyl carbon of aldehydes or ketones in the presence of *strictly anhydrous* electrophilic trapping agents.[6b,6c]

Table 1. Crystallographic Data and Data Collection Parameters for $(MeO)CH(C_6H_5)P^+(C_6H_5)_2(C_6H_4SO_3^-)$

formula	$C_{27}H_{27}O_5PS$
fw	494.5
space group	monoclinic, $P2_1/c$ (No. 14)
a, Å	10.039 (5)
b, Å	31.797 (8)
c, Å	7.510 (3)
β, deg	100.59 (4)
V, Å^3	2356.6 (15)
Z	4
d (calcd), g/cm^3	1.394
abs coeff, mm^{-1}	0.233
λ, Å	0.71073
T, K	193
R,[a] %	6.91
R_w,[a] %	6.30

[a] $R = \sum|F_o - F_c|/\sum F_o$. $R_w = [[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]]^{1/2}$.

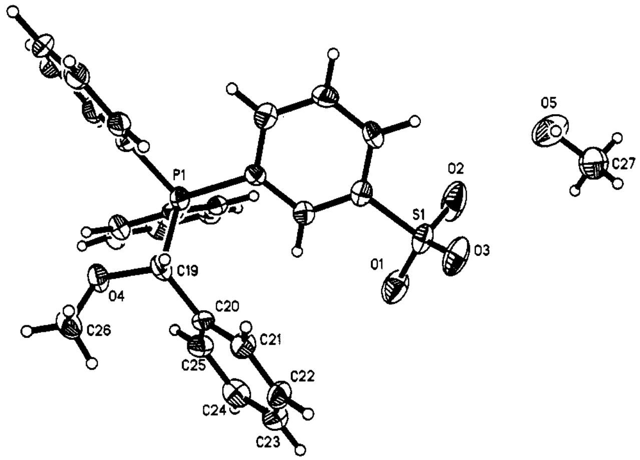

Figure 1. ORTEP view of $(MeO)CH(C_6H_5)P^+(C_6H_5)_2(C_6H_4SO_3^-)$ with ellipsoids drawn at the 50% probability level.

In this paper, we wish to report upon the instantaneous reaction between TPPMS and aldehydes in an aqueous solution.

Experimental Section

General Procedures. All reactions were carried out under an inert atmosphere with degassed solvents. NMR spectra were collected using both a Varian XL-200E (^1H) and a Varian XL200 (^{31}P) spectrometers. All chemicals were obtained commercially without further purification.

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(1) (a) Texas A&M University. (b) Kossuth Lajos University.

(2) (a) Joó, F.; Tóth Z. *J. Mol. Catal.* **1980**, *8*, 369. (b) Kuntz, E. G. *CHEMTECH* **1987**, *17*, 570. (c) Sinou, D. *Bull. Soc. Chim. Fr.* **1987**, 480. (d) Kalck, P.; Monteil, F. *Adv. Organomet. Chem.* **1992**, *34*, 219. (e) Russell, M. J. H.; *Platinum Met. Rev.* **1988**, *32*, 179. (f) Herrmann, W. A.; Kohlpaintner, C. W. *J. Mol. Catal.* **1992**, *73*, 191.

(3) (a) Lensink, C.; deVries, J. G.; *Tetrahedron: Asymmetry* **1992**, *3*, 235. (b) Amrani, Y.; Lecomte, L.; Sinou, D.; Bakos, J.; Tóth, I.; Heil, B. *Organometallics* **1989**, *8*, 542. (c) Sinou, D.; Safi, M.; Claver, C.; Masdeu, A. *J. Mol. Catal.* **1991**, *68* , L9.

(4) (a) Tóth, Z.; Joó, F.; Beck, M. T. *Inorg.. Chim. Acta* **1980**, *42*, 153. (b) Fache, E.; Santini, C.; Senocq, F.; Basset, J. M. *J. Mol. Catal.* **1992**, *72*, 331.

(5) (a) Laghmari, Sinou, D. *J. Mol. Catal.* **1991**, *66*, L15. (b) Okano, T.; Kaji, M.; Isotani, S.; Kiji, J. *Tetrahedron Lett.* **1992**, *33*, 5547. (c) Bényei, A.; Joó, F. *J. Mol. Catal.* **1990**, *58*, 151. (d) Horváth, I. T.; Kastrup, R. V.; Oswald, A. A.; Mozeleski, E. J. *Catal. Lett.* **1990**, *2*, 85.

(6) (a) Barton, D. H. R.; Ollis, W. D., Eds. *Comprehensive Organic Chemistry* Pergamon Press: New York, 1979; Vol. 2, pp 1147–1160. (b) Lee, S. W.; Trogler, W. C. *J. Org. Chem.* **1990**, *55*, 2644. (c) Dal Canto, R. A.; Roskamp, E. J. *J. Org. Chem.* **1992**, *57*, 406.

(7) Larpent, C.; Patin, H. *Tetrahedron* **1988**, *44*, 6107.

(8) (a) Bényei, A.; Stafford, J. N. W.; Kathó, A.; Darensbourg, D. J.; Joó, F. *J. Mol. Catal.* **1993**, *84*, 157. (b) Joó, F.; Somsák, L.; Beck. M. T. *Mol. Catal.* **1984**, *24*, 71.

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $C_{27}H_{27}O_5PS$

	x	*y*	*z*	$U(eq)^{a,b}$
S(1)	4886(1)	3725(1)	6668(2)	33(1)
P(1)	1058(1)	3722(1)	302(2)	23(1)
O(1)	4201(4)	4127(1)	6703(6)	52(2)
O(2)	4658(4)	3456(2)	8147(6)	63(2)
O(3)	6273(4)	3757(1)	6471(5)	48(2)
O(4)	778(3)	4319(1)	-2069(5)	32(1)
O(5)	6230(5)	2831(2)	9993(7)	72(2)
C(1)	2341(5)	3462(2)	1926(7)	21(2)
C(2)	3045(5)	3678(2)	3454(7)	25(2)
C(3)	4011(5)	3465(2)	4668(7)	25(2)
C(4)	4296(5)	3042(2)	4398(8)	29(2)
C(5)	3600(6)	2834(2)	2906(8)	34(2)
C(6)	2621(6)	3040(2)	1677(7)	31(2)
C(7)	451(5)	3366(2)	-1548(7)	26(2)
C(8)	-892(6)	3228(2)	-1888(7)	31(2)
C(9)	-1315(6)	2958(2)	-3317(8)	40(2)
C(10)	-418(7)	2820(2)	-4369(8)	39(2)
C(11)	904(6)	2958(2)	-4017(7)	35(2)
C(12)	1343(6)	3231(2)	-2634(7)	28(2)
C(13)	-322(5)	3896(2)	1347(7)	23(2)
C(14)	-314(6)	3832(2)	3174(7)	26(2)
C(15)	-1418(6)	3955(2)	3927(8)	32(2)
C(16)	-2506(6)	4147(2)	2841(8)	37(2)
C(17)	-2504(6)	4218(2)	1038(8)	38(2)
C(18)	-1429(5)	4095(2)	258(7)	28(2)
C(19)	1832(5)	4168(2)	-687(7)	28(2)
C(20)	2442(5)	4496(2)	690(7)	24(2)
C(21)	3833(5)	4555(2)	1030(7)	30(2)
C(22)	4404(6)	4861(2)	2206(8)	34(2)
C(23)	3614(6)	5108(2)	3077(8)	38(2)
C(24)	2229(6)	5057(2)	2756(8)	37(2)
C(25)	1625(6)	4751(2)	1536(7)	31(2)
C(26)	1278(6)	4604(2)	-3275(8)	39(2)
C(27)	6816(7)	3016(2)	11639(8)	52(3)

[a] Estimated standard deviations are given in parentheses. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Preparation of Phosphonium Salts. The phosphonium salts were prepared by dissolving equimolar amounts of TPPMS and aldehyde in ethanol and then adding 1 equiv of aqueous HCl. The resulting solution was filtered to obtain a crystal clear solution and then evaporated *in vacuo*. The resulting white highly hygroscopic solid dissolved cleanly in $CHCl_3$ as well as water. The salts were characterized in water by ^{31}P NMR as follows: pentanal 20.8 ppm; hexanal 20.7 ppm; heptanal 20.6 ppm; benzaldehyde 21.2 ppm; salicylaldehyde 20.1 ppm; dihydrocinnamaldehyde 20.5 ppm; cinnamaldehyde 20.6 ppm. These complexes were also characterized by ^1H NMR. Elemental analyses were not obtained due to the extreme hygroscopic nature of the phosphonium salts.

Synthesis of TPPMS-benzaldehyde Adduct and Crystal Growth. To 400 mg of TPPMS (1 mmol) and 0.90 mL of 1.2 M HCl was added 15 mL of wet ethanol at 60 °C. Then 102 mg of benzaldehyde (1 mmol) was added in 3 mL of ethanol. The solution was allowed to cool, and the product was isolated by evaporation of the solvent *in vacuo*. The residue was recrystallized from chloroform, and the adduct was characterized by ^1H and ^{31}P NMR (^1H NMR C–H 6.6 ppm (d), aromatic protons 7–8.5 ppm (m), O–H 10.1 ppm (s); ^{31}P NMR 21.2 ppm). Crystals were obtained by dissolution of the phosphonium salt in methanol.

X-ray Structure of $(MeO)CH(C_6H_5)P^+(C_6H_5)_2(C_6H_4SO_3^-)$. A colorless parallelepiped (0.24 mm × 0.26 mm × 0.26 mm) was mounted on a glass fiber with epoxy cement at room temperature and cooled to 193 K in a N_2 cold stream. Preliminary examination and data collection were performed on a Siemens R3m/V X-ray diffractometer (oriented graphite monochromator; Mo Kα λ = 0.710 73 Å radiation).[9a] Cell parameters were calculated from the least-squares fitting of the setting angles for 25 reflections. ω scans for several intense reflections indicated acceptable crystal quality.[9b]

Data was collected for $4° \leq 2\theta \leq 50°$ (ω (Wyckoff) scans, $-11 \leq h \leq 11$, $0 \leq k \leq 37$, $-8 \leq l \leq 0$) at 193 K. Scan width on ω was 1.00°, with a variable scan rate of 2.00–14.65° min^{-1}. Three control reflections, collected every 97 reflections, showed no significant trends. Background measurement by stationary crystal/stationary counter technique was taken at the beginning and end of each scan for half of the total scan time.

Table 3. Bond Lengths (Å) for $C_{27}H_{27}O_5PS$

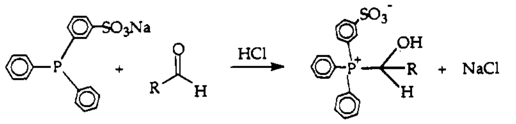
S(1)–O(1)	1.453 (5)	S(1)–O(2)	1.453 (5)
S(1)–O(3)	1.431 (4)	S(1)–C(3)	1.797 (5)
P(1)–C(1)	1.803 (5)	P(1)–C(7)	1.807 (5)
P(1)–C(13)	1.800 (6)	P(1)–C(19)	1.840 (6)
O(4)–C(19)	1.423 (6)	O(4)–C(26)	1.434 (7)
O(5)–C(27)	1.398 (8)	C(1)–C(2)	1.409 (7)
C(1)–C(6)	1.391 (8)	C(2)–C(3)	1.380 (7)
C(3)–C(4)	1.395 (8)	C(4)–C(5)	1.377 (8)
C(5)–C(6)	1.384 (7)	C(7)–C(8)	1.397 (8)
C(7)–C(12)	1.386 (8)	C(8)–C(9)	1.380 (8)
C(9)–C(10)	1.38 (1)	C(10)–C(11)	1.376 (9)
C(11)–C(12)	1.364 (8)	C(13)–C(14)	1.386 (8)
C(13)–C(18)	1.403 (7)	C(14)–C(15)	1.389 (9)
C(15)–C(16)	1.380 (8)	C(16)–C(17)	1.373 (9)
C(17)–C(18)	1.377 (9)	C(19)–C(20)	1.515 (7)
C(20)–C(21)	1.386 (7)	C(20)–C(25)	1.389 (8)
C(21)–C(22)	1.368 (8)	C(22)–C(23)	1.366 (9)
C(23)–C(24)	1.377 (9)	C(24)–C(25)	1.396 (8)

[a] Estimated standard deviations are given in parentheses.

Lorentz and polarization corrections were applied to 4566 reflections. No absorption correction was applied. A total of 2439 unique reflections, with $|I| \geq 2.0\,\sigma(I)$, were used in further calculations. The structure was solved by direct methods.[9c] Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $R = 0.069$, $R_w = 0.063$, and $S = 1.58$ at convergence. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 $Å^3$. Neutral atom scattering factors and anomalous scattering correction terms were taken from a standard source.[9d] Crystal data and experimental conditions are provided in Table 1.

Results and Discussion

The water-soluble (1-hydroxyalkyl)phosphonium salts formed by the nucleophilic addition of TPPMS to aldehydes were characterized primarily by ^{31}P NMR following acidification (eq 2). That is, upon the addition of stoichiometric amounts of various



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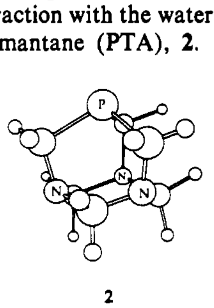
aldehydes the characteristic singlet for TPPMS at –5.5 ppm disappears and a new singlet appears at lower field around 20 ppm. An analogous reaction occurs between TPPTS and benzaldehyde in acidic media. For instance, in 6% HCl/D_2O the addition of benzaldehyde results in 87% of the initial phosphine reacting to form the phosphonium salt, as confirmed by the partial disappearance of the TPPTS peak and the formation of a new peak at 20.9 ppm in the ^{31}P NMR. Both peaks are fairly broad indicating a reversible equilibrium is occurring. We did not observe such an interaction with the water-soluble ligand 1,3,5-triaza-7-phosphaadamantane (PTA), 2. The mechanism for



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(9) (a) Control software, P3VAX 3.42, was supplied by Nicolet Analytical X-ray Instruments, Madison, WI. (b) ω scans were recorded graphically for several intense reflections, along each principle axis. Crystal quality was determined by inspection of the peak profiles and their spread in ω. (c) All crystallographic calculations were performed with SHELXTL-PLUS rev 3.4. (d) Ibers, J. A., Hamilton, W. S., Eds. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table 4. Bond Angles (deg) for $C_{27}H_{27}O_5PS$

O(1)–S(1)–O(2)	111.2 (3)	O(1)–S(1)–O(3)	114.4 (3)
O(2)–S(1)–O(3)	114.5 (3)	O(1)–S(1)–C(3)	105.0 (2)
O(2)–S(1)–C(3)	104.3 (3)	O(3)–S(1)–C(3)	106.4 (3)
C(1)–P(1)–C(7)	109.4 (2)	C(1)–P(1)–C(13)	110.9 (2)
C(7)–P(1)–C(13)	110.5 (2)	C(1)–P(1)–C(19)	108.9 (2)
C(7)–P(1)–C(19)	106.3 (3)	C(13)–P(1)–C(19)	110.8 (3)
C(19)–O(4)–C(26)	111.9 (4)	P(1)–C(1)–C(2)	121.2 (4)
P(1)–C(1)–C(6)	119.2 (4)	C(2)–C(1)–C(6)	119.6 (5)
C(1)–C(2)–C(3)	119.1 (5)	S(1)–C(3)–C(2)	120.2 (4)
S(1)–C(3)–C(4)	118.9 (4)	C(2)–C(3)–C(4)	120.9 (5)
C(3)–C(4)–C(5)	119.6 (5)	C(4)–C(5)–C(6)	120.4 (5)
C(1)–C(6)–C(5)	120.3 (5)	P(1)–C(7)–C(8)	121.0 (4)
P(1)–C(7)–C(12)	118.9 (4)	C(8)–C(7)–C(12)	120.1 (5)
C(7)–C(8)–C(9)	119.2 (6)	C(8)–C(9)–C(10)	120.3 (6)
C(9)–C(10)–C(11)	119.9 (5)	C(10)–C(11)–C(12)	121.0 (6)
C(7)–C(12)–C(11)	119.5 (5)	P(1)–C(13)–C(14)	121.5 (4)
P(1)–C(13)–C(18)	118.3 (4)	C(14)–C(13)–C(18)	120.2 (5)
C(13)–C(14)–C(15	120.1 (5)	C(14)–C(15)–C(16)	119.2 (5)
C(15)–C(16)–C(17)	120.7 (6)	C(16)–C(17)–C(18)	121.1 (5)
C(13)–C(18)–C(17)	118.6 (5)	P(1)–C(19)–O(4)	104.0 (3)
P(1)–C(19)–C(20)	113.7 (4)	O(4)–C(19)–C(20)	114.8 (4)
C(19)–C(20)–C(21)	119.1 (5)	C(19)–C(20)–C(25)	121.1 (5)
C(21)–C(20)–C(25)	119.8 (5)	C(20)–C(21)–C(22)	120.2 (5)
C(21)–C(22)–C(23)	120.6 (5)	C(22)–C(23)–C(24)	120.3 (5)
C(23)–C(24)–C(25)	120.0 (6)	C(20)–C(25)–C(24)	119.1 (5)

[a] Estimated standard deviations are given in parentheses.

formation of these salts is probably analogous to that reported by Lee and Trogler.[6b]

X-ray quality crystals of the benzaldehyde-TPPMS adduct were obtained from a methanolic solution as a methyl ether (Figure 1). This complex crystallized in the monoclinic space group $P2_1/c$. The data collection parameters are given in Table 1. Atomic positional parameters and selected bond lengths and angles are collected in Tables 2–4. The unit cell dimensions were determined to be a = 10.039(5) Å, b = 31.797(8) Å, c = 7.510(3) Å, β = 100.59(4)°, V = 2356.6 (15) $Å^3$, and d = 1.394 g cm^{-3} for Z = 4. The bond distance to the methoxy carbon P(1)–C(19) (1.840(6) Å) is slightly longer than the three other P–C bond distances (1.803 Å average). This difference is not as significant as that found for $[(CH_3)_2C(OH)PEt_3]Br$ of 0.08 Å.[6b] A packing diagram shows a two-dimensional network of hydrogen bonds between a sulfonate oxygen and the H–O of a solvent methanol molecule (O(2)–O(5) = 2.750 Å) (Figure 2). There is no close contact between the positively charged phosphorus atom and the negative oxygen centers of the sulfonate moiety, with the nearest P···O distance being 4.31 Å.

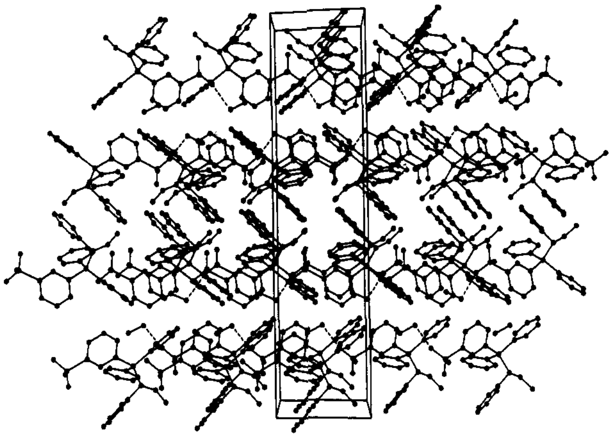

Figure 2. Packing diagram for $(MeO)CH(C_6H_5)P^+(C_6H_5)_2(C_6H_4SO_3^-)$.

In principle, all reactions catalyzed by phosphine complexes and involving aldehydes, including their formation in processes, i.e. hydroformylation, may be influenced by such an interaction. This reaction can lead to severe phosphine loss and may account in part for the large excess phosphine requirement in these catalytic processes. Obviously, the ion solvating power (polarity) and protic nature of a solvent will influence the formation of phosphonium salts via protonation of the anionic intermediate and hence may influence the selectivity and activity of these processes. Therefore, such interactions should be included in mechanistic considerations of these catalytic reactions, particularly for catalytic systems in protic solvents. Indeed the use of the PTA ligand for the preparation of water-soluble complexes may be very beneficial since it does not readily form these phosphonium salts.

Acknowledgment. The financial support of this research by the National Science Foundation (Grants CHE91-19737 and INT90-08227) and Hungarian Academy of Science (30.008/134/90) and the Hungarian National Research Foundation (OTKA T7527) is greatly appreciated. Ágnes Kathó is grateful for a travel grant from the Széchenyi Foundation, Budapest, Hungary.

Supplementary Material Available: Tables of anisotropic thermal parameters and H-atom coordinates for $(MeO)CH(C_6H_5)P^+(C_6H_5)_2(C_6H_4SO_3^-)$ (4 pages). Ordering information is given on any current masthead page.