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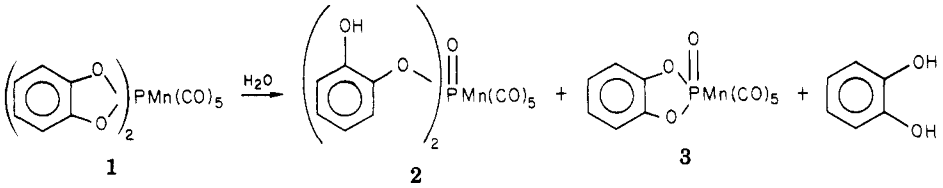
Reactivity of Transition-Metal-Substituted Phosphoranes: Spectroscopic and X-ray Crystal Structural Study of the Hydrolysis of Pentacarbonyl(2,2′-spirobi[1,3,2-benzodioxaphosphol-2-yl])manganese

Michael Lattman,*[†] Badri N. Anand,[†] Shirley S. C. Chu,*[‡] and Robert D. Rosenstein[‡]

Departments of Chemistry and Electrical Engineering, Southern Methodist University, Dallas, Texas 75275

Received August 9, 1983

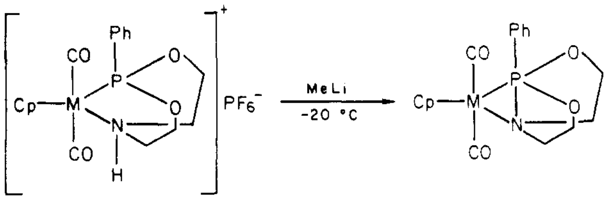
The hydrolysis of the title compound is found to proceed according to the reaction



The hydrolysis reactions in solution lead initially to two phosphorus-containing species, 2 and 3. 2 is found to rearrange to 3 and catechol in solution. The crystal structure of 2, $(o\text{-}HOC_6H_4O)_2P(O)Mn(CO)_5$, was determined, and it belongs to the tetragonal system with a space group of $I4_1/a$. The unit cell parameters are $a = 25.145$ (10) and $c = 12.025$ (5) Å and $Z = 16$. The phosphoryl oxygen is linked to two hydroxyl groups with one intramolecular and one intermolecular hydrogen bond.

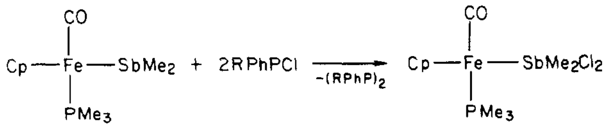
Introduction

Metalated derivatives of pentacoordinate P, As, and Sb are rare and comprise (i) bridging, polycyclic systems[1] and (ii) nonbridging, simple metal-substituted derivatives.[2] Riess and co-workers[1] have synthesized molecules of type i as illustrated in reaction 1. Malisch and co-workers[2a] reported the first member of type ii according to reaction 2. Previous work[2b] from this laboratory has led to the synthesis of pentacarbonyl(2,2′-spirobi[1,3,2-benzodioxaphosphol-2-yl])manganese (1) according to reaction 3. Subsequently, another member of this class of molecules has been reported, synthesized by oxidative addition of dichlorine to a metal-substituted phosphine.[2c]



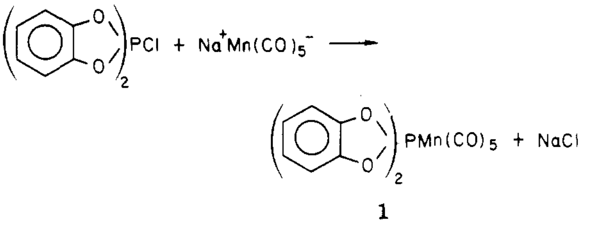
(1)

M = Mo, W; Ph = phenyl; Cp = η^5-C_5H_5



(2)

R = Ph, Me



(3)

Besides syntheses of transition-metal compounds with high-valent ligands, we are interested in their reactivity, both at the metal and at the hypervalent atom center. This paper reports the hydrolysis reactions of 1 under a variety of conditions. These reactions were studied to determine the hydrolytic stability of 1 and to compare the products of hydrolysis of 1 to hydrolysis products of main-group oxyphosphoranes already present in the literature.[3-5] The reactions presented here were studied by IR as well as ^{13}C and ^{31}P NMR techniques. The X-ray crystal structure of one of the hydrolysis products is reported in this paper.

Results

1 is a slightly yellow solid which can be handled in the atmosphere for short periods of time. It decomposes under

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[†] Department of Chemistry.

[‡] Department of Electrical Engineering.

[1] (a) Jeanneaux, F.; Grand, A.; Riess, J. G. *J. Am. Chem. Soc.* **1981**, *103*, 4272. (b) Wachter, J.; Mentzen, B. F.; Riess, J. G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 284. (c) Dupart, J. M.; Grand, A.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 2316.

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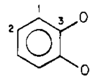
[4] McClelland, R. A.; Patel, G.; Cirinna, C. *J. Am. Chem. Soc.* **1981**, *103*, 6432.

[5] Westheimer, F. H. *Chem. Rev.* **1981**, *81*, 313.

Table I. NMR Data[a] for Compound 1 and Hydrolysis Products A and B

compd/ hydrolysis product	^{31}P	$^{13}C\{^1H\}$[b]
1	67	110.6 (C_1)[c] (J_{POCC} = 6.8 Hz), 121.4 (C_2),[c] 147.0 (C_3)[c] (J_{POC} = 4.2 Hz)
A	120	112.2[d] (J = 4.6 Hz),[e] 116.0,[f] 120.3,[f] 122.8,[d] 146.3,[f] 147.2[d]
B	112	119.1, 120.2, 123.4, 126.1, 142.3 (J = 14.3 Hz), 149.8

[a] All data obtained in THF. ^{31}P chemical shifts referenced to external H_3PO_4. ^{13}C chemical shifts measured relative to solvent peaks (referenced to Me_4Si). [b] All ^{13}C spectra show a broad peak centered at ca. 206 ppm due to CO. [c] Assigned as



in accordance with the assignments for catechol in ref 7. [d] Assigned to 3 (see text). [e] J_{POCC} (see text). [f] Assigned to catechol (see text).

vacuum at ca. 70 °C.[6] When 1 is allowed to react with H_2O in a 1:1 molar ratio in ether a white precipitate appears within an hour. After 24 h the solid is separated and dissolved in THF to record its spectra. Initially, the ^{31}P NMR spectrum shows two broad peaks at 120 and 112 ppm, while the $^{13}C\{^1H\}$ spectrum is complex in the phenyl region.. Upon standing in THF solution, the 112 ppm peak in the ^{31}P spectrum gradually disappears and is completely gone after 3 days. The resulting ^{13}C spectrum has simplified to six peaks in the aromatic region: two in the C–O (ca. 145 ppm) and four in the C–H (ca. 120 ppm) region[7] (see product A in Table I). If a sample of pure catechol is added to this solution, the ^{13}C peaks at 116.0, 120.2, and 146.3 ppm are observed to increase in intensity.

If the hydrolysis is done in THF, similar results are observed. Peaks at 112 and 120 ppm appear in the ^{31}P spectrum as the 67 ppm peak diminishes, while new peaks appear in the ^{13}C spectrum. After 4 days, the observed spectra are that of product A.[8]

Exposure of 1 to air as a solid also leads to spectral changes, though more slowly than in solution. After 24 h, a THF solution of the exposed solid shows only unreacted starting material in the ^{31}P spectrum. After 7–10 days, reaction in the solid state is complete. When the resulting solid is dissolved in THF, it initially shows only one peak in the ^{31}P spectrum at 112 ppm and six peaks in the ^{13}C spectrum, two in the C–O and four in the C–H regions. However, these are at different chemical shifts from those of product A obtained from the solution hydrolyses (see product B in Table I). Within 1 h spectral changes in this solution are evident. Peaks due to A begin to appear in the NMR spectra. After 24 h, all of the peaks due to B have vanished and only the peaks due to A are present in both spectra. Similar behavior is observed in CH_2Cl_2 solution.

Finally, concentration of the solution of product A from the THF hydrolysis (or from the above rearrangement) affords crystals which, when separated, dried, and redissolved in THF, yield the 120 ppm ^{31}P peak and only the 112.2, 122.8, and 147.2 ppm ^{13}C peaks.

Scheme I

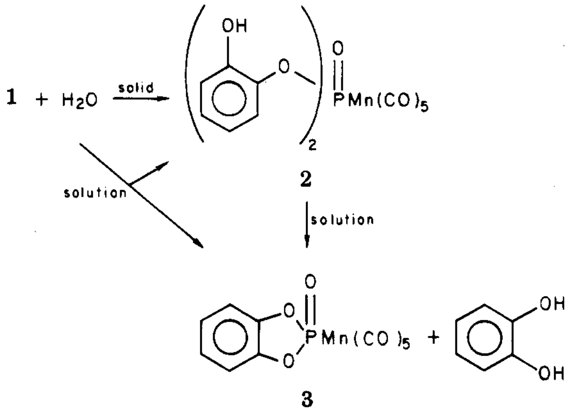


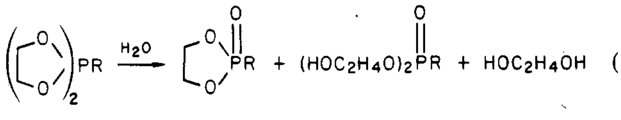
Table II. IR Spectra[a] of 1, 2, and 3 in the CO Stretching Region

1[b]	2	3[c]
2133 (m)	2138 (m)	2134 (m)
2075 (w, sh)	2076 (w, sh)	2074 (w, sh)
2041 (vs)	2045 (vs)	2038 (vs)
2003 (m, sh)		2008 (m, sh)

[a] Data obtained in THF solution. [b] Data from ref 2b. [c] Data obtained from a sample of 3 crystallized from solution A (see text).

Discussion

Hydrolysis Reactions. From the above data it is apparent that two phosphorus-containing species are formed from hydrolysis, and only one of them is the thermodynamically favored product. Since peaks due to catechol are present in product A it is likely that the reactions follow the general pathway outlined in Scheme I. This pathway is supported by the following. First, 2, pentacarbonylbis(2-hydroxyphenoxy)phosphinylmanganese, and 3, pentacarbonyl(2-oxo-1,3,2λ^5-benzodioxaphosphol-2-yl)manganese, would be expected to have ^{31}P chemical shifts in the same region.. Also, 2 should have six peaks in the ^{13}C phenyl region, and 3 should have three, as found. Second, previous data[4] on the hydrolysis of cyclic oxyphosphoranes shown the hydrolysis of $(\overline{OC_2H_4O})_2PR$ (R = $4\text{-}CH_3C_6H_4$, C_6H_5, $4\text{-}ClC_6H_4$) to proceed according to reaction 4. Third, since the $PMn(CO)_5$ fragment remains intact, the IR spectra of 1, 2, and 3 should be similar in the CO stretching region, as is evident from the data in Table II. Finally, the structure of 2 has been determined by X-ray crystallography and is reported in the following section.



(4)

At this point it is difficult to rationalize the detailed mechanism or mechanisms of the reactions. For example, is 3 formed exclusively from 2 or also directly from 1? The fact that 2 is the only product in the solid state may support the former path, though different mechanisms could very well be involved in the solid and solution processes. Previous mechanistic studies on the hydrolysis of oxyphosphoranes show the hydrolysis of $(C_6H_5O)_5P$[3] to proceed via an associative mechanism over all pH ranges, while the hydrolysis of $(\overline{OC_2H_4O})_2PR$ (reaction 4) proceeds

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[6] 1 turns slightly green over prolonged periods of storage under nitrogen in the dark. Presumably some oxidation occurs, but IR and NMR spectra of the green compound are identical with spectra obtained from freshly prepared and purified 1.

[7] See spectra of mono- and disubstituted RO– derivatives of benzene in, for example: Johnson, L. F.; Jankowski, W. C. "Carbon-13 NMR Spectra"; Wiley: New York, 1972.

[8] A few small-intensity impurity peaks are present in the ^{31}P spectrum.

Table III. Bond Lengths (Including Hydrogen Bonds) (Å) and Bond Angles (deg)[a]

Bond Lengths

Mn-P	2.297 (2)	C(1')-O(1')	1.364 (7)
Mn-C(1)	1.844 (6)	C(6')-O'(P)	1.398 (6)
Mn-C(2)	1.869 (6)	C(1'')-O(1'')	1.373 (7)
Mn-C(3)	1.851 (6)	C(6'')-O''(P)	1.405 (6)
Mn-C(4)	1.865 (6)	C(1')-C(2')	1.374 (9)
Mn-C(5)	1.836 (6)	C(1')-C(6')	1.400 (8)
P-O(P)	1.487 (4)	C(2')-C(3')	1.388 (10)
P-O'(P)	1.606 (4)	C(3')-C(4')	1.366 (11)
P-O''(P)	1.617 (4)	C(4')-C(5')	1.372 (10)
C(1)-O(1)	1.143 (7)	C(5')-C(6')	1.377 (9)
C(2)-O(2)	1.124 (8)	C(1'')-C(2'')	1.383 (8)
C(3)-O(3)	1.136 (7)	C(1'')-C(6'')	1.380 (8)
C(4)-O(4)	1.125 (7)	C(2'')-C(3'')	1.372 (8)
C(5)-O(5)	1.142 (7)	C(3'')-C(4'')	1.389 (8)
O(1')-H(O1')	0.98 (9)	C(4'')-C(5'')	1.371 (8)
O(1'')-H(O1'')	0.85 (9)	C(5'')-C(6'')	1.362 (8)

O(P)[*x*,*y*,*z*]---H(O1')[−0.25 + *y*, 0.75 − *x*, −0.25 + *z*]	1.75 (9)
O(P)[*x*,*y*,*z*]---H(O1'')[*x*,*y*,*z*]	2.01 (9)
O(P)[*x*,*y*,*z*]---O(1')[−0.25 + *y*, 0.75 − *x*, −0.25 + *z*]	2.650 (5)
O(P)[*x*,*y*,*z*]---O(1'')[*x*,*y*,*z*]	2.831 (6)

Bond Angles

C(1)-Mn-P	85.6 (2)	O(1')-C(1')-C(2')	123.8 (5)
C(1)-Mn-C(2)	89.8 (3)	O(1')-C(1')-C(6')	117.0 (5)
C(1)-Mn-C(3)	90.8 (2)	C(2')-C(1')-C(6')	119.1 (5)
C(1)-Mn-C(4)	174.7 (3)	C(1')-C(2')-C(3')	119.4 (6)
C(1)-Mn-C(5)	92.9 (2)	C(2')-C(3')-C(4')	121.1 (7)
C(2)-Mn-P	85.8 (2)	C(3')-C(4')-C(5')	120.1 (7)
C(2)-Mn-C(3)	174.9 (3)	C(4')-C(5')-C(6')	119.5 (6)
C(2)-Mn-C(4)	92.7 (3)	O'(P)-C(6')-C(1')	119.1 (5)
C(2)-Mn-C(5)	93.2 (3)	O'(P)-C(6')-C(5')	120.2 (5)
C(3)-Mn-P	89.1 (2)	C(1')-C(6')-C(5')	120.6 (5)
C(3)-Mn-C(4)	86.3 (2)	O(1'')-C(1'')-C(2'')	118.6 (5)
C(3)-Mn-C(5)	91.9 (3)	O(1'')-C(1'')-C(6'')	122.5 (5)
C(4)-Mn-P	90.0 (2)	C(2'')-C(1'')-C(6'')	118.9 (5)
C(4)-Mn-C(5)	91.6 (3)	C(1'')-C(2'')-C(3'')	120.2 (5)
C(5)-Mn-P	178.2 (2)	C(2'')-C(3'')-C(4'')	119.8 (5)
Mn-P-O(P)	117.4 (2)	C(3'')-C(4'')-C(5'')	120.1 (6)
Mn-P-O'(P)	112.7 (2)	C(4'')-C(5'')-C(6'')	119.6 (5)
Mn-P-O''(P)	104.0 (2)	O''(P)-C(6'')-C(1'')	118.8 (5)
O(P)-P-O'(P)	110.8 (2)	O''(P)-C(6'')-C(5'')	119.4 (5)
O(P)-P-O''(P)	109.4 (2)	C(1'')-C(6'')-C(5'')	121.4 (5)
O'(P)-P-O''(P)	100.9 (2)	C(2')-C(1')-O(1')	123.8 (5)
P-O'(P)-C(6')	124.7 (3)	C(6')-C(1')-O(1')	117.0 (5)
P-O''(P)-C(6'')	123.6 (3)	C(2'')-C(1'')-O(1'')	118.6 (5)
O(P)---H(O1')-O(1')	151 (8)	C(6'')-C(1'')-O(1'')	122.5 (5)
O(P)---H(O1'')-O(1'')	164 (8)	C(1')-O(1')-H(O1')	108 (5)
		C(1'')-O(1'')-H(O1'')	104 (6)

[a] The estimated standard deviations are given in parentheses and refer to the last positions of respective values.

via an associative route only in base.[4] We support an associative mechanism for the reaction involved here, i.e., proceeding through hexacoordinate phosphorus.

It is interesting to note the trend in $^{31}P-^{13}C$ coupling constants. In 1, $J_{POCC} > J_{POC}$. This is also found in the precursor to 1, $(\overline{OC_6H_4O})_2PCl$, where J_{POCC} = 19.4 Hz and J_{POC} = 7.6 Hz. In fact, this trend is observed in many molecules with POCC linkages[9] and is consistent with the assignment of the observed coupling constant of 3 (Table I, A) to J_{POCC}; J_{POC} is apparently too small to be detected. However, an unequivocal assignment of the observed coupling constant in 2 (Table I, B) cannot be made.

Crystal Structure of 2. The identification of the atoms and the configuration of the molecule are shown in the ORTEP drawing[10] in Figure 1. The bond lengths and bond angles, with their standard deviations, are shown in Table III. The P and Mn atoms have distorted tetrahedral and octahedral configurations, respectively. The Mn–P bond length of 2.297 (2) Å is in line with the 2.25–2.30-Å values found in the only other known manganese phosphonate structure (of a hexanuclear metal cluster), $Mn_6(CO)_9[OP(OC_2H_5)_2]_9$.[11] There exist two hydrogen

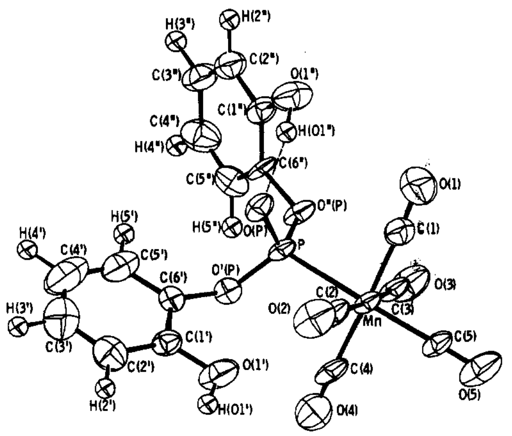

Figure 1. ORTEP drawing of one molecule of 2. The hydrogen atoms are drawn with an arbitrary scale.

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(9) See, for example, spectra 358, 383, 384, 451, 476, and 500 in ref 7.

(10) Johnson, C. K. "ORTEP, Report ORNL-3784" Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Table IV. Torsion Angles (deg) about the Mn-P Bond in 2

C(1)-Mn-P-O(P)	−47.2 (3)	C(3)-Mn-P-O′(P)	91.3 (3)
C(2)-Mn-P-O(P)	42.9 (3)	C(4)-Mn-P-O′(P)	5.0 (2)
C(3)-Mn-P-O(P)	−138.1 (2)	C(1)-Mn-P-O″(P)	73.7 (2)
C(4)-Mn-P-O(P)	135.6 (2)	C(2)-Mn-P-O″(P)	163.9 (2)
C(1)-Mn-P-O′(P)	−177.8 (2)	C(3)-Mn-P-O″(P)	−17.1 (2)
C(2)-Mn-P-O′(P)	−87.7 (3)	C(4)-Mn-P-O″(P)	−103.4 (2)

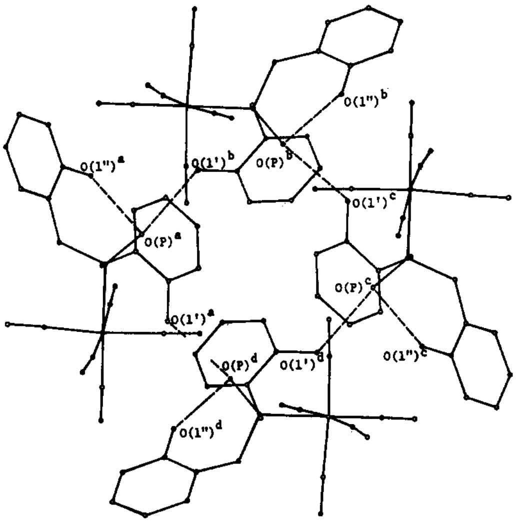

Figure 2. The intramolecular and intermolecular hydrogen bonds (indicated by dashed lines) shown by four of the molecules related by 4_1 symmetry with symmetry operations as indicated by the superscripts. (a) *x*, *y*, *z*; (b) −0.25 + *y*, 0.75 − *x*, −0.25 + *z*; (c) 0.50 − *x*, 1.00 − *y*, −0.50 + *z*; (d) 0.75 − *y*, 0.25 + *x*, −0.75 + *z*.

bonds in one asymmetric unit of the crystal of 2, one intramolecular and one intermolecular, as shown in Figure 2. The intermolecular hydrogen bonds lead to a chain arrangement of molecules related by the 4_1 axis. The phosphoryl oxygen is linked intramolecularly to one hydroxyl group, O(1″), and intermolecularly to the other hydroxyl group, O(1′). The packing of the molecules in the crystal is determined mainly by the hydrogen bonds and there are no other close intermolecular contacts.

A number of transition-metal phosphonate structures have been reported.[11-19] Most of these compounds exhibit some donor properties by the phosphoryl oxygen, either hydrogen bonding or metal binding. The P=O bond length varies from 1.44 to 1.53 Å; however, no correlation has been found between the P=O bond length and the nature of the secondary bonding of the phosphoryl oxygen. The P=O bond length of 1.487 (4) Å in 2 is the same as that found in η^5-$C_5H_5Cr(CO)_2[OP(OCH_3)_2]P(OCH_3)_3$.[13] While the phosphoryl oxygen in 2 is involved with two hydrogen bonds, the phosphoryl oxygen in the Cr complex does not involve any secondary interactions. The two benzene rings are planar and the two planes are nearly perpendicular with a dihedral angle of 87.4 (2)°. The four equatorial carbonyl carbons (C(1), C(2), C(3), and C(4)) lie on a plane; however, the equatorial carbonyl oxygens deviate from the plane toward the side with the phosphorus and the manganese atom deviates from the plane toward the axial carbonyl group. This is similar to many compounds of the type $LM(CO)_5$ and $LM(CO)_4$ where the equatorial carbonyl groups are bent toward the L group.[20] In 2 the average C_{eq}–Mn–P bond angle is 87.6°.

The torsion angles about the Mn–P bond are given in Table IV. The P=O bond is found to have a staggered conformation with respect to the C(1)—Mn and C(2)—Mn bonds, while the two hydroxyphenyl groups have different conformations with respect to the P=O bond. These are apparently the result of the intra- and intermolecular hydrogen-bonding interactions.

Summary

We have studied the hydrolytic reactivity of one of the first members of a new class of compounds: transition-metal-substituted phosphoranes. The reactivity of 1 parallels the reactivity of main-group oxyphosphoranes, and the P–Mn bond does not appear to be particularly labile (at least toward hydrolysis). However, the rearrangement reaction observed for 2 appears unique to the metallosubstituted species. The X-ray crystal structure of 2 reveals strong and extensive hydrogen bonding which is probably a factor in its solid-state stability. We are continuing to study the reactivity of 1 toward other reagents in order to determine if there is any effect due to the hypervalent phosphorus–metal bond.

Experimental Section

THF was distilled from sodium/benzophenone, anhydrous ether was dried over sodium ribbon, and reagent grade CH_2Cl_2 was used without further purification. All solvents were deoxygenated before use. All reactions were carried out under an atmosphere of nitrogen or argon unless otherwise stated. 1 was prepared as described previously.[2b] IR and NMR spectra were recorded in THF solutions on a Perkin-Elmer 283 infrared spectrometer and IBM WP200SY multinuclear NMR. All ^{13}C spectra were ^1H decoupled. Elemental analyses were done by Galbraith Laboratories, Knoxville, TN.

Hydrolysis in Ether. In a typical reaction 1.79 g (4.05 mmol) of 1 was dissolved in 100 mL of ether. To this stirred solution 73.0 μL (4.05 mmol) of distilled water was syringed in. After 24 h the white solid that had formed was allowed to settle and the supernatant liquid syringed out. The solid was washed once with 4 mL of ether and dried under vacuum.

Hydrolysis in THF. In a typical experiment 0.438 g (0.991 mmol) of 1 was dissolved in 3.0 mL of THF in an 8-mm NMR tube; 17.9 μL (0.991 mmol) of distilled water was syringed into this solution. After 5 days the volume was reduced by two-thirds, leading to the formation of crystals. The supernatant solution was syringed off, and the crystals were washed quickly with THF

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Table V. Crystal and Experimental Data of $(o\text{-HOC}_6\text{H}_4\text{O})_2\text{P(O)Mn(CO)}_5$ (2)

chemical formula	$C_{17}H_{10}O_{10}PMn$
formula wt	460.17
cryst system	tetragonal
space group	$I4_1/a$
systematic absences	hkl absent with $h + k + l$ odd $hk0$ absent with h odd (k odd) $00l$ absent with $l \neq 4n$
unit cell dimens	a = 25.145 (10) Å c = 12.025 (5) Å V = 7603 (3) Å^3
temp for unit cell meas and data collection	T = 165 K
density (calcd)	1.608 g cm^{-3}
no. of molecules per unit cell	16
X-radiation used for data collection	λ(Cu Kα) = 1.5418 Å
linear abs coeff	μ(Cu Kα) = 72.5 cm^{-1}
total no. of reflcns with $2\theta < 130°$	2013
no. of reflcns with $I > 3\sigma(I)$	1512
disagreement index, $R = (\Sigma \| F_o | F_c \| / \Sigma | F_o |)$	0.046 for 1512 reflcns
R_w	0.047
cryst size	0.3 × 0.3 × 0.3 mm
weighting scheme	$w = 1/[\sigma^2(F) + qF^2]$ (q) = 0.0008 in the final refinement cycle

and dried under vacuum to yield 0.203 g (59%) of 3. Anal. Calcd for $C_{11}H_4MnO_8P$: C, 37.74; H, 1.15; P, 8.85. Found: C, 37.82; H, 1.29; P, 8.92.

X-ray Analysis. Suitable crystals of 2 were grown by slow hydrolysis of a solution of 1 in ether and sealed in a thin-walled quartz tube for data collection. The unit-cell parameters and intensity data were measured at 165 K on a Syntex P2$_1$ computer-controlled diffractometer. The crystal data are summarized in Table V. A $\theta/2\theta$ scanning mode with graphite monochromatic Cu Kα radiation was used in the intensity measurements. A reflection was considered as observed if the intensity, I, was greater than five times its standard deviation, $\sigma(I)$, and the standard deviation was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors, and the absorption corrections were applied by using SHELX 76.[21]

Structure Determination. The structure was determined by the application of direct methods and was refined by using the SHELX 76[21] system of programs. The refinement was carried out by the full-matrix least-squares method with anisotropic temperature factors for non-hydrogen atoms. The hydrogen positions were located on a difference Fourier synthesis. Isotropic temperature factors were used for the hydrogen atoms, and the positional parameters were varied with constraints on the C–H bond distances. The weighting scheme was $w = 1/[\sigma^2(F) + qF^2]$, where $\sigma(F)$ is the standard deviation of the structure amplitude as derived from counting statistics and q is a parameter to be adjusted after each cycle; its final value was $q = 0.0008$. Reflections with I less than $3\sigma(I)$ were excluded from the refinement. In addition, 20 low-order strong reflections, whose calculated structure amplitudes were much larger than the observed values, were also excluded from the refinement. The final disagreement index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|)$, was 0.046 for 1512 reflections. The atomic scattering factors used for manganese, phosphorus, oxygen, carbon, and hydrogen atoms were taken from ref 22.

Acknowledgment. The generous financial support of the Robert A. Welch Foundation (M.L. and S.S.C.C.), Research Corporation (M.L.), and S.M.U. (Seed Grant, M.L.) are gratefully acknowledged. B.N.A. thanks Panjab University, Chandigarh, India, for granting a leave of absence.

Registry No. 1, 85269-90-5; 2, 89121-17-5; 3, 89121-18-6.

Supplementary Material Available: Tables of final positional parameters, anisotropic thermal parameters, least squares planes, and structure factors (11 pages). Ordering information is given on any current masthead page.

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(21) Sheldrick, G. M. "SHELX. Program for Crystal Structure Determination"; University of Cambridge: Cambridge, England, 1976.

(22) "International Table for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.