Bicyclic Phosphite Esters from Pentaerythritol and Dipentaerythritol: New Bridging Ligands in Organometallic and Inorganic Chemistry

Robert D. Pike,*,† Bryn A. Reinecke,† Megan E. Dellinger,† Austin B. Wiles,†
Jonathan D. Harper,† Jenine R. Cole,† Kimberly A. Dendramis,† Brian D. Borne,†
Jeffrey L. Harris,‡ and William T. Pennington‡

Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23187, and
Department of Chemistry, Clemson University, Clemson, South Carolina 29634

Received January 15, 2004

Transesterification reactions yield bicyclic (caged) phosphite esters $P(OCH_2)_3CCH_2OH$ (**1**) and $(P(OCH_2)_3CCH_2)_2O$ (**2**), and $P(OCH_2)_3CCH_2O_2CR$ (R = Ph, **3**; 4-$^tBuC_6H_4$, **4**; 4-$O_2NC_6H_4$, **5**; 3-pyridyl, **6**; 4-pyridyl, **7**; $^1/_2$ p-C_6H_4, **8**; $^1/_2$ m-C_6H_4, **9**; $^1/_3$ 1,3,5-C_6H_3, **10**), which can act as ligands. Metal-bridged complexes and X-ray structures of **7**, $\{[(\eta^5\text{-MeCp})Mn(CO)_2]_2(\mu\text{-}\mathbf{2})\}$ (**11**), and $[CuBr(\mathbf{2})]_\infty\cdot MeCN$ (**12**) are reported.

Introduction

Phosphite esters have long been of interest as ligands in organometallic chemistry and have recently attracted increased attention as alternatives to phosphine ligands in metal-based catalysts.[1] However, phosphites suffer from several potential decomposition and rearrangement reactions, including hydrolysis, alcoholysis, fairly facile oxidation to phosphates, and rearrangement to form phosphonates. One strategy to limit these problems (except that of oxidation) is the use of bicyclic (caged) phosphites, $P(OCH_2)_3CR$. Originally reported by Verkade[2] and by Wadsworth and Emmons,[3] these species have found only limited application as ligands in metal complexes.[4] Nevertheless, in addition to their improved stability, the "tied back" ring structure of caged phosphite ligands gives rise to increased π-acidity[5] and minimal cone angles of about 101°.[6]

The attachment of two or more caged phosphite groups to relatively rigid molecular frameworks should produce polydentate ligands well suited to the formation of metal-organic networks, a rapidly expanding and potentially rich field of investigation.[7] Moreover, the high π-acidity of such ligands should favor the formation of networks incorporating low-valent metals, such as are important in catalytic coupling reactions. Therefore, we set out to produce bis(caged phosphite) esters from pentaerythritol and dipentaerythritol according to the reactions shown in Scheme 1. Some phosphorus esterifications of these polyols has previously been described in the patent literature,[8] and phosphites **1** and **3** have been mentioned in the open literature, but without synthetic details.[9]

Results and Discussion

Synthesis of Phosphites. Caged phosphites **1** and **2** were prepared via transesterification reactions of $P(OPh)_3$ with pentaerythritol and dipentaerythritol,

---

* Corresponding author. Tel: 757-221-2555. Fax: 757-221-2715. E-mail: rdpike@wm.edu.

† College of William and Mary.

‡ Clemson University.

(1) (a) Baker, M. J.; Harrison, K. N.; Orpen, A. G.; Pringle, P. G.; Shaw, G. *J. Chem. Soc., Chem. Commun.* **1991**, 803. (b) Cuny, G. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2066. (c) Higashizima, T.; Sakai, N.; Nozaki, K.; Takaya, H. *Tetrahedron Lett.* **1994**, *35*, 2023. (d) Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869. (e) van Rooy, A.; Orij, E. N.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1995**, *14*, 34. (f) Moasser, B.; Gladfelter, W. L.; Roe, D. C. *Organometallics* **1995**, *14*, 3832. (g) Bedford, R. B.; Castillòn, S.; Chaloner, P. A.; Claver, C.; Fernandez, E.; Hitchcock, P. B.; Ruiz, A. *Organometallics* **1996**, *15*, 3990. (h) Pastor, S. D.; Rogers, J. S.; NabiRahni, M. A.; Stevens, E. D. *Inorg. Chem.* **1996**, *35*, 2157. (i) Buisman, G. J. H.; van der Veen, L. A.; Klootwijk, A.; de Lange, W. G. J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Vogt, D. *Organometallics* **1997**, *16*, 2929. (j) Diéguez, M.; Ruiz, A.; Claver, C. *J. Org. Chem.* **2002**, *67*, 3796. (k) Shum, S. P.; Pastor, S. D.; DeBellis, A. D.; Odorisio, P. A.; Burke, L.; Clarke, F. H.; Rihs, G.; Piatek, B.; Rodebaugh, R. K. *Inorg. Chem.* **2003**, *42*, 5097.

(2) Verkade, J. G.; Reynolds, L. T. *J. Org. Chem.* **1960**, *25*, 663.

(3) Wadsworth, W. S., Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1962**, *84*, 610.

(4) (a) Verkade, J. G.; Piper, T. S. *Inorg. Chem.* **1962**, *1*, 453. (b) Verkade, J. G.; Piper, T. S. *Inorg. Chem.* **1963**, *2*, 944. (c) Verkade, J. G.; McCarley, R. E.; Hendricker, D. G.; King, R. W. *Inorg. Chem.* **1965**, *4*, 228. (d) Huttemann, T. J., Jr.; Foxman, B. M.; Sperati, C. R.; Verkade, J. G. *Inorg. Chem.* **1965**, *4*, 950. (e) Vandenbroucke, A. C., Jr.; Hendricker, D. G.; McCarley, R. E.; Verkade, J. G. *Inorg. Chem.* **1968**, *7*, 1825. (f) Coskran, K. J.; Jenkins, J. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1968**, *90*, 5437. (g) Hyde, E. M.; Swain, J. R.; Verkade, J. G.; Meakin, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1169. (h) Honig, E. D.; Quin-jin, M.; Robinson, W. T.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1985**, *4*, 871. (i) Fang, X.; Scott, B. L.; John, K. D.; Kubas, G. J. *Organometallics* **2000**, *19*, 4141. (j) Cole, J. R.; Dellinger, M. E.; Johnson, T. J.; Reinecke, B. A.; Pike, R. D.; Pennington, W. T.; Krawiec, M.; Rheingold, A. L. *J. Chem. Crystallogr.* **2003**, *33*, 341.

(5) McEwen, G. K.; Rix, C. J.; Traynor, M. F.; Verkade, J. G. *Inorg. Chem.* **1974**, *13*, 2800.

(6) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

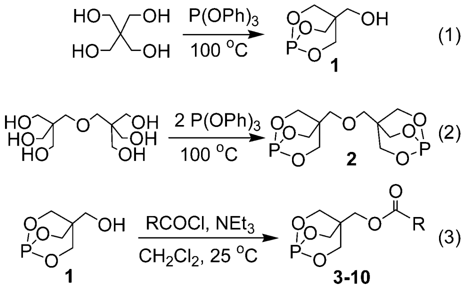
(7) (a) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305. (b) Forster, P. M.; Cheetham, A. K. *Top. Catal.* **2003**, *24*, 79. (c) Janiak, C. *Dalton Trans.* **2003**, 2781. (d) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (e) Braga, D.; Maini, L.; Polito, M.; Scaccianoce, L.; Cojazzi, G.; Grepioni, F. *Coord. Chem. Rev.* **2001**, *216−217*, 225.

(8) (a) Baranauckas, C. F.; Gordon, I. U.S. Patent 3,310,609, 1967; *Chem. Abstr.* 1967, 473142. (b) Baranauckas, C. F.; Gordon, I. U.S. Patent 3,511,857, 1970; *Chem. Abstr.* 1970, 426205. (c) Hechenbleikner, I. U.S. Patent 3,737,485, 1973; *Chem. Abstr.* 1973, 443288. (d) Baranauckas, C. F.; Gordon, I. U.S. Patent 3,801,677, 1974; *Chem. Abstr.* 1974, 404062. (e) Schwarzenbach, K.; Gilg, B.; Brunetti, H.; Mueller, H. Ger. Offen. 2,431,623, 1975; *Chem. Abstr.* 1975, 480421. (f) Fischer, E.; Mayer, N.; Pfahler, G. Ger. Offen. 2,506,207, 1976; *Chem. Abstr.* 1976, 576865.

(9) (a) Voorhees, K. J.; Hileman, F. D.; Smith, D. L. *Org. Mass Spectrom.* **1979**, *14*, 459. (b) Ramos, S. M.; Owrutsky, J. C.; Keehn, P. M. *Tetrahedron Lett.* **1985**, *26*, 5895.

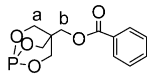
10.1021/om049957r CCC: $27.50

Scheme 1

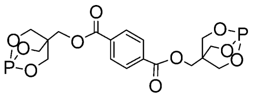


respectively, as shown in eqs 1 and 2, Scheme 1. These reactions are particularly convenient for a number of reasons: (1) They are carried out under solventless conditions in sealed tubes and can be easily done on multigram scales. (2) The starting materials are inexpensive. (3) The byproduct PhOH is lost from the reaction mixture via spontaneous sublimation onto the walls of the reaction tube. After recrystallization, ether **2** is obtained as a free-flowing, analytically pure white powder. On the other hand, alcohol product **1** forms as a clear, colorless syrup that is not easily handled. Instead, the further esterification of **1** can be undertaken in situ (see below). In contrast to the ease of the transesterification reactions 1 and 2, the syntheses of **1** and **2** using PCl_3/NEt_3 proved to be inconvenient, necessitating an emulsion-prone extraction step and yielding at best only traces of product.

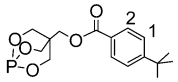
The remaining hydroxyl site on **1** can be exploited via the further esterification reactions (3) with acid chlorides in the presence of base (Scheme 1). Thus, upon addition of a NEt_3/CH_2Cl_2 mixture, the syrupy **1** converts to an opaque semisolid, which reacts readily on addition of a $RCOCl/CH_2Cl_2$ mixture. Stirring or refluxing the mixture in the resealed tube produces fair to good yields of esters **3**−**10**. Following extraction the products are isolated as white solids.



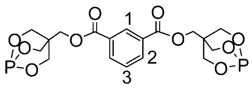
3



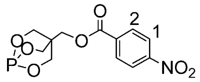
8



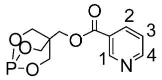
4



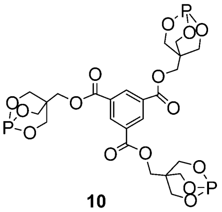
9



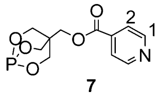
5



6



10



7

An X-ray crystal structure of **7** was solved. Crystallographic data are listed in Table 1, and the structure is shown in Figure 1. All bond lengths and angles for **7** were found to be within typical ranges. The rigid 4-pyridyl and caged phosphite groups are aligned in opposite directions along the polar *b*-axis. The separation between P1 and N1 of 9.258 Å represents the bridge length for this potential ligand.

Metal-Phosphite Complexes. The new polyphosphites and pyridyl phosphites **2** and **6**−**10** have significant potential as network-forming ligands. The bridging ligand behavior of **2** was demonstrated by coordination to the $[(\eta^5\text{-MeCp})Mn(CO)_2]$ fragment. Photolytic carbonyl substitution of $[(\eta^5\text{-MeCp})Mn(CO)_3]$ (2 equiv) with **2** (1 equiv) produced complex **11**, as confirmed by IR spectroscopy. The NMR signals of **2** were shifted downfield very slightly upon coordination to the metal. Single-crystal X-ray determination of **11** was undertaken, and the resulting structure is presented in Figure 2. Crystallographic data are listed in Table 1. The structure of **11** confirmed the expected bridged dimer configuration with each metal center having piano stool geometry and linear carbonyl ligands. The Mn−P bonds are shorter than that in the other crystallographically determined Mn-caged phosphite complex, *cis*-$[Mn(CO)_4(\eta^2\text{-cyclooctene})(P(OCH_2)_3CMe)]^+$.[4i] The shorter bond in the present example is most likely the result of stronger phosphite π-back-bonding from the more electron-rich neutral metal center. The effect of the small caged phosphite cone angle is apparent upon examination of the bond angles around the manganese atoms. Thus the C1−Mn2−C2 angle (92.5°) is not compressed with respect to C1−Mn2−P1 (88.8°) and C2−Mn2−P1 (92.7°). The caged diphosphite **2** has a bridge length (P1···P2) of 9.251 Å in **11**. The bridging angle for **2** was assessed by determining the angle between nonbonded vectors P1···C11 and P2···C12; this angle is 111.9°. The combined effects of the length and bend angle of **2** result in a substantial Mn1···Mn2 separation of 12.831 Å.

Preliminary studies involving the bridging caged phosphites have demonstrated their ability to form insoluble networks with low-valent metal centers. The Ni(0) products, $[Ni(P(OPh)_3)_2(\mathbf{2})]$, $[Ni(P(OPh)_3)_3(\mathbf{2})_{1/2}]$, and $[Ni(P(OPh)_3)_3(\mathbf{10})_{1/3}]$, have been formed by partial ligand substitution of $[Ni(P(OPh)_3)_4]$. Reactions of CuX (X = Cl, Br, I) with **2** have led to products identified as $[CuX(\mathbf{2})]$ and $[(CuI)_2(\mathbf{2})]$. Prolonged heating of $[CuBr(\mathbf{2})]$ (**12**) in acetonitrile at 100 °C produced crystals from which an X-ray structure was solved. The molecular and layer structures are presented in Figures 3 and 4. Crystallographic data are listed in Table 1. The copper centers are linked by the ligand into infinite chains, with adjacent units related by a *c*-glide operation $(1 + x, {}^1/_2 - y, {}^1/_2 - z)$. The chains are cross-linked through Cu_2Br_2 dimer[10] formation about inversion centers $({}^1/_2, 0, {}^1/_2)$. The resulting layers consist of tiled tetrameric macrocyclic units that contain the acetonitrile solvent molecules. There are no apparent directed interactions between the solvent molecules and the layers. The layers stack along the (1 0 −2) direction. The ligand bridge length (P1···P2) is 8.763 Å in **12**, somewhat shorter than that in **11** despite a larger bridging angle (see discussion above) of 115.7°. The bridged Cu1···Cu1A distance is 12.712 Å, slightly shorter than the Mn···Mn separation in **11**. Further studies of these and similar network solids are in progress.

---

[10] The structural coordination chemistry of CuX is dominated by Cu_2X_2 dimers and $(CuX)_\infty$ chains; see refs 11 and 12 and the citations therein.

Table 1. Crystallographic Data for 7, 11, and 12

	7	11	12
empirical formula	$C_{11}H_{12}NO_5P$	$C_{26}H_{30}Mn_2O_{11}P_2$	$C_{12}H_{19}BrCuNO_7P_2$
fw	269.19	690.32	494.67
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$C2/c$	$P2_1/c$
unit cell dimens	$a = 6.276(3)$ Å $b = 10.223(5)$ Å $c = 9.694(5)$ Å $\beta = 100.407(12)°$	$a = 15.0246(15)$ Å $b = 12.0315(10)$ Å $c = 32.234(3)$ Å $\beta = 92.179(5)°$	$a = 10.192(3)$ Å $b = 16.512(5)$ Å $c = 10.833(3)$ Å $\beta = 99.621(9)°$
volume	611.7(5) Å^3	5822.6(9) Å^3	1805.7(9) Å^3
Z	2	8	4
density(calcd)	1.461 Mg/m^3	1.575 Mg/m^3	1.828 Mg/m^3
abs coeff	0.237 mm^{-1}	1.035 mm^{-1}	3.649 mm^{-1}
cryst size	0.21 × 0.28 × 0.34 mm	0.15 × 0.10 × 0.10 mm	0.16 × 0.07 × 0.05 mm
θ range for data collection	4.11 to 26.75°	2.17 to 27.51°	2.03 to 30.59°
no. of reflns collected	6018	12 330	17 371
no. of indep reflns	2529 [R(int) = 0.0151]	5504 [R(int) = 0.0458]	3662 [R(int) = 0.071]
goodness-of-fit on F^2	1.125	1.054	1.052
final R indices [$I > 2\sigma(I)$]	R1 = 0.0382, wR2 = 0.0963	R1 = 0.0766, wR2 = 0.1577	R1 = 0.0601, wR2 = 0.1500

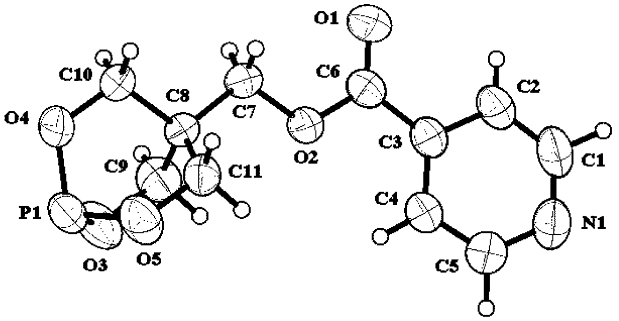


Figure 1. Molecular structure of **7**. The displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: P1−O4 1.6067(18), O1−C6 1.201(3), O2−C6 1.342(2), O2−C7 1.445(3), O4−C10 1.437(3), C3−C6 1.486(3), C7−C8 1.514(3), C8−C10 1.532(3). Selected bond angles [deg]: O3−P1−O4 101.10(11), C6−O2−C7 115.09(16), C10−O4−P1 117.29(14), O1−C6−O2 123.4(2), O1−C6−C3 124.25(19), O2−C6−C3 112.36(16), O2−C7−C8 108.18(15), C7−C8−C10 108.10(16), C11−C8−C10 106.71(18), O4−C10−C8 110.66(16).

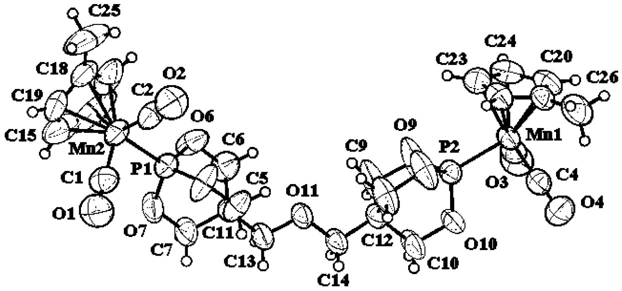


Figure 2. Molecular structure of **11**. The displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Mn1−C4 1.757(8), Mn1−C3 1.768(7), Mn1−P2 2.1377(2), Mn2−C1 1.775(8), Mn2−C2 1.777(8), Mn2−P1 2.1340(19), O1−C1 1.147(8), O2−C2 1.140(8), O3−C3 1.164(7), O4−C4 1.169(8). Selected bond angles [deg]: C4−Mn1−C3 91.9(3), C4−Mn1−P2 92.5(2), C3−Mn1−P2 91.1(2), C1−Mn2−C2 92.5(3), C1−Mn2−P1 88.8(2), C2−Mn2−P1 92.7(2), O1−C1−Mn2 178.8(8), O2−C2−Mn2 176.3(7), O3−C3−Mn1 179.7(7), O4−C4−Mn1 177.9(7).

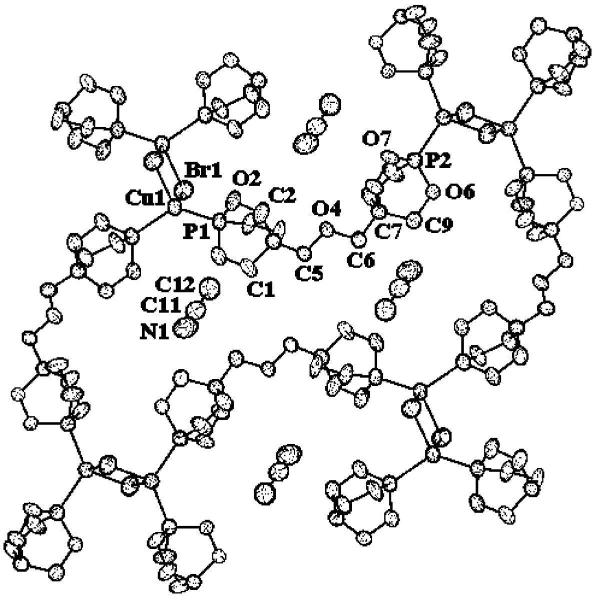


Figure 3. Molecular structure of **12**. The displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted. Selected bond lengths [Å]: Br1−Cu1 2.4617(12), Br1−Cu1A 2.4896(12), Cu1−P1 2.2011(19) Cu1−P2A 2.218(2), Cu1···Cu1A 2.9359(18). Selected bond angles [deg]: Cu1−Br1−Cu1A 72.73(4), P1−Cu1−P2A 124.89(8), P1−Cu1−Br1 109.57(6), P2A−Cu1−Br1 105.48(6), P1−Cu1−Br1A 109.37(6), P2A−Cu1−Br1A 98.81(6), Br1−Cu1−Br1A 107.27(4).

Conclusion

A series of caged phosphite ligands are readily prepared from pentaerythritol and dipentaerythritol via transesterification reactions. Some of these phosphites can act as bidentate bridging ligands and therefore can act as network-forming ligands for low-valent metal centers. The formation of a bimetallic Mn(I) complex **11** and a polymeric Cu(I) network **12** demonstrates the bridging behavior of **2**.

Experimental Section

Materials. The starting materials and solvents were purchased from commercial suppliers and were used without purification, except for the following: THF was purified by passing through alumina and molecular sieves and then degassed prior to use. CuCl and CuBr were recrystallized from HCl and HBr, respectively. [$Ni(P(OPh)_3)_4$] was prepared via reduction of $Ni(NO_3)_2 \cdot 6H_2O$ with $^nBu_4NBH_4$ in DMAc solvent. Anal. Calcd for $C_{72}H_{60}NiO_{12}P_4$: C, 66.53; H, 4.65. Found: C, 66.53; H, 4.69.

4-Hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane (1). In a 30.5 (length) × 38.1 (i.d.) cm pressure tube (Ace 8648) were loaded $P(OPh)_3$ (10.69 g, 34.5 mmol) and

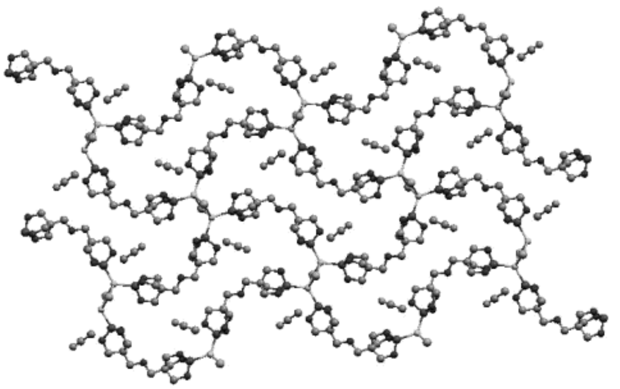


Figure 4. Layer structure of **12**. Hydrogen atoms are omitted.

pentaerythritol (4.69 g, 34.4 mmol), forming a slurry. The tube was sealed with a Teflon screw cap and immersed to a depth of about 3 cm in a 100 °C oil bath. After about 3 h, a seed crystal of PhOH was adhered to the inside wall of the tube, causing crystallization to commence. After 1 day, the clear liquid mixture was frozen in liquid N_2 and the PhOH was scraped from the walls of the tube and weighed. After another day at 100 °C, more PhOH was scraped out of the tube. The total PhOH collected was 8.85 g (94.0 mmol, 91.1% of theory). After one more day at 100 °C, the last traces of PhOH were removed by careful rinsing with acetone. The product remained on the bottom of the tube as a clear, colorless syrup (5.37 g, 32.7 mmol, 95.1%). It was usually not isolated, but rather further esterified as described below. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.07 (d, $J = 1.9$ Hz, 6H, H^a), 3.33 (s, 2 H, H^b). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 69.1, 62.6 (d, $J = 5.6$ Hz), 37.4 (d, $J = 22.4$ Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 93.9. Anal. Calcd for $C_5H_9O_4P$: C, 36.60; H, 5.53. Found: C, 37.23; H, 5.66. EI-MS m/z (relative intensity): 164 (M$^+$, 16), 134 (14), 116 (4), 70 (100).

Bis(4-methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane) Ether (2). In a pressure tube were loaded $P(OPh)_3$ (9.96 g, 32.1 mmol) and dipentaerythritol (4.08 g, 16.0 mmol), forming a slurry. The tube was sealed with a Teflon screw cap and immersed to a depth of about 3 cm in a 100 °C oil bath. After about 3 h, a seed crystal of PhOH was adhered to the inside wall of the tube, causing crystallization to commence. After 1 day, the clear liquid mixture was frozen in liquid N_2 and the PhOH was scraped from the walls of the tube and weighed. After another day at 100 °C, the product mixture was an opaque solid and more PhOH was scraped out of the tube. The total PhOH collected was 7.42 g (78.9 mmol, 82.1% of theory). After 2 more days at 100 °C, a small amount more PhOH was removed by careful rinsing with acetone. About 30 mL of $CHCl_3$ was added to the solid product, and the tube was resealed and reheated to 100 °C. After 3 h the clear, colorless solution was filtered and the solvent was removed under vacuum. The resulting white solid was suspended and stirred in about 30 mL of fresh Et_2O four times and then collected via filtration (3.67 g, 11.8 mmol, 73.9%). Mp: 153−155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.01 (d, $J = 2.0$ Hz, 12H, H^a), 3.01 (s, 4 H, H^b). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 71.6 (d, $J = 6.1$ Hz), 68.9, 37.0 (d, $J = 23.0$ Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 94.2. Anal. Calcd for $C_{10}H_{16}O_7P_2$: C, 38.72; H, 5.20. Found: C, 38.63; H, 5.20. EI-MS m/z (relative intensity): 310 (M$^+$, 34), 217 (100), 199 (9), 152 (14), 77 (51).

4-Methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane Benzoate (3). Into a pressure tube containing **1** (30.6 mmol) at 25 °C was added NEt_3 (3.18 g, 31.4 mmol) dissolved in CH_2Cl_2 (25 mL). The tube was capped and sonicated for 5 min, forming a semisolid suspended mass. The tube was opened and PhCOCl (4.32 g, 30.7 mmol) dissolved in CH_2Cl_2 (25 mL) was added. The tube was capped and sonicated for 30 min. The resulting solution was filtered and then extracted twice each with $NaHCO_3$(aq), NaCl(aq), and H_2O. The CH_2Cl_2 layers were combined and dried over $MgSO_4$. After filtration, the solvent was removed under vacuum, leaving the product as a white solid (3.53 g, 13.2 mmol, 43.1%). Mp: 143−146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, $J = 8.4$ Hz, 2H, o-Ph), 7.60 (t, $J = 7.4$ Hz, 1H, p-Ph), 7.46 (t, $J = 7.8$ Hz, 2H, m-Ph), 4.17 (d, $J = 2.0$ Hz, 6H, H^a), 4.00 (s, 2H, H^b). ^{13}C-{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.9, 133.9, 129.8, 129.1, 128.8, 68.9, 63.7 (d, $J = 6.1$ Hz), 36.5 (d, $J = 23.0$ Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 93.9. Anal. Calcd for $C_{12}H_{13}O_5P$: C, 53.74; H, 4.89. Found: C, 52.34; H, 4.84. EI-MS m/z (relative intensity): 268 (M$^+$, 18), 175 (7), 146 (9), 116 (19), 105 (100), 77 (28).

4-Methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane 4-*tert*-Butylbenzoate (4). This compound was prepared according to a method analogous to that for **3** (20.9% yield). Mp: 153−156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, $J = 8.4$ Hz, 2H, H^2), 7.48 (d, $J = 8.8$ Hz, 2H, H^1), 4.17 (d, $J = 2.0$ Hz, 6H, H^a), 4.00 (s, 2H, H^b), 1.34 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.9, 157.7, 129.7, 126.3, 125.8, 68.9, 63.4 (d, $J = 6.1$ Hz), 36.4 (d, $J = 23.0$ Hz), 35.5, 31.4. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 93.4. Anal. Calcd for $C_{16}H_{21}O_5P$: C, 59.26; H, 6.53. Found: C, 57.54; H, 6.52. EI-MS m/z (relative intensity): 161 (45), 145 (57), 116 (94), 103 (24), 91 (82), 77 (100).

4-Methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane 4-Nitrobenzoate (5). This compound was prepared according to a method analogous to that for **3** (37.3% yield). Mp: 184−187 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, $J = 8.9$ Hz, 2H, H^1), 8.17 (d, $J = 8.9$ Hz, 2H, H^2), 4.18 (d, $J = 2.0$ Hz, 6H, H^a), 4.08 (s, 2H, H^b). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ 164.1, 150.9, 134.7, 131.2, 124.0, 68.7, 64.5 (d, $J = 7.2$ Hz), 36.3 (d, $J = 23.8$ Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 93.7. Anal. Calcd for $C_{12}H_{12}NO_7P$: C, 46.02; H, 3.86; N, 4.47. Found: C, 45.97; H, 4.07; N, 4.26. EI-MS m/z (relative intensity): 313 (M$^+$, 2), 220 (7), 150 (100), 146 (12), 116 (12), 104 (12), 76 (11).

4-Methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane Nicotinoate (6). This compound was prepared according to a method analogous to that for **3** (24.5% yield). Mp: 145−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (s, 1H, H^1), 8.83 (d, $J = 4.7$ Hz, 1H, H^4), 8.26 (d, $J = 8.6$ Hz, 1H, H^2), 7.45 (dd, $J = 8.0$, 4.9 Hz, 1H, H^3), 4.19 (d, $J = 1.2$ Hz, 6H, H^a), 4.07 (s, 2H, H^b). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.7, 154.2, 150.9, 137.2, 125.2, 123.7, 68.7, 64.0 (d, $J = 6.1$ Hz), 36.5 (d, $J = 23.8$ Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 93.1. Anal. Calcd for $C_{11}H_{12}NO_5P$: C, 49.08; H, 4.49; N, 5.20. Found: C, 47.53; H, 4.73; N, 4.94. EI-MS m/z (relative intensity): 146 (4), 115 (12), 106 (100), 78 (74).

4-Methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane Isonicotinoate (7). This compound was prepared according to a method analogous to that for **3**, except that the mixture was heated overnight (47.2% yield). X-ray quality crystals were grown by liquid diffusion of pentane into a solution of **7** in Et_2O. Mp: 119−122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (dd, $J = 4.5$, 1.8 Hz, 2H, H^1), 7.80 (dd, $J = 4.5$, 1.8 Hz, 2H, H^2), 4.18 (d, $J = 2.0$ Hz, 6H, H^a), 4.06 (s, 2H, H^b). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.5, 151.0, 136.3, 122.9, 68.6, 64.4 (d, $J = 6.1$ Hz), 36.3 (d, $J = 23.0$ Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 93.1. Anal. Calcd for $C_{11}H_{12}NO_5P$: C, 49.08; H, 4.49; N, 5.20. Found: C, 48.65; H, 4.53; N, 5.24. EI-MS m/z (relative intensity): 269 (M$^+$, 14), 240 (6), 211 (8), 176 (8), 146 (17), 116 (15), 106 (100), 78 (28).

Bis(4-methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane) Terephthalate (8). This compound was prepared according to a method analogous to that for **3**, using 2 equiv of **1** for each equivalent of p-$C_6H_4(COCl)_2$ (49.5% yield). Mp: 181−184 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 4H, C_6H_4), 4.17 (d, $J = 1.7$ Hz, 12H, H^a), 4.05 (s, 4H, H^b). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.9, 133.5, 130.0, 68.7, 64.2 (d, $J =$

5.5 Hz), 36.4 (d, $J = 23.6$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 93.7. Anal. Calcd for $C_{18}H_{20}O_{10}P_2$: C, 47.17; H, 4.40. Found: C, 48.24; H, 4.53.

Bis(4-methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane) Isophthalate (9). This compound was prepared according to a method analogous to that for **3**, using 2 equiv of **1** for each equivalent of m-$C_6H_4(COCl)_2$ (26.7% yield). Mp: >250 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H, H^1), 8.21 (dd, $J = 7.8$, 1.4 Hz, 2H, H^2), 7.61 (t, $J = 7.4$ Hz, 1H, H^3), 4.18 (d, $J = 1.9$ Hz, 12H, H^a), 4.07 (s, 4H, H^b). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 165.1, 134.8, 130.4, 130.3, 122.5, 68.8, 64.3 (d, $J = 5.5$ Hz), 36.3 (d, $J = 23.8$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 93.2. Anal. Calcd for $C_{18}H_{20}O_{10}P_2$: C, 47.17; H, 4.40. Found: C, 47.76; H, 4.80.

Tris(4-methylene-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane) 1,3,5-Benzenetricarboxylate (10). This compound was prepared according to a method analogous to that for **3**, using 3 equiv of **1** for each equivalent of 1,3,5-$C_6H_3(COCl)_3$ (64.3% yield). Mp: 140−143 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 3H, C_6H_3), 4.19 (d, $J = 2.0$ Hz, 18H, H^a), 4.13 (s, 6H, H^b). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.9, 135.1, 130.9, 68.7, 64.5 (d, $J = 6.9$ Hz), 36.6 (d, $J = 23.8$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 93.0. Anal. Calcd for $C_{24}H_{27}O_{15}P_3$: C, 44.46; H, 4.20. Found: C, 45.20; H, 4.42.

{**Bis[(dicarbonyl)(η^5-methylcyclopentadienyl)manganese(I)](bis(4-methylene-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane) Ether)**} **(11).** [(η^5-MeCp)Mn$(CO)_3$] (0.302 g, 1.38 mmol) and **2** (0.206 g, 0.664 mmol) were dissolved in 25 mL of THF under N_2. The yellow mixture was refluxed under visible incandescent light. After 3 days, IR analysis showed 90% conversion. The clear orange-brown solution was evaporated under vacuum. Fractional crystallization from CH_2Cl_2/Et_2O produced a pale yellow powder (0.187 g, 0.271 mmol, 40.8%). X-ray quality crystals were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of **11**. Mp: ca. 165 °C (dec). IR $\nu_{C\equiv O}$ (CH_2Cl_2, cm^{-1}): 1965, 1892. ^1H NMR (400 MHz, $CDCl_3$): δ 4.42 (s, 8H, Cp), 4.24 (d, $J = 2.7$ Hz, 12H, H^a), 3.07 (s, 4H, H^b), 1.93 (s, 6H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 228.6, 228.2, 100.1, 81.6, 80.6, 72.6 (d, $J = 6.9$ Hz), 70.7, 37.2 (d, $J = 32.2$ Hz). Anal. Calcd for $C_{26}H_{30}Mn_2O_{11}P_2$: C, 45.24; H, 4.38. Found: C, 45.06; H, 4.40.

Copper(I) Halide Complexes. CuX (2.00 mmol) was dissolved in 35 mL of MeCN under N_2. Phosphite **2** (2.00 mmol) dissolved in 20 mL of MeCN was added via syringe. A white precipitate formed almost immediately. The solid was collected by filtration after 30 min stirring at room temperature and was washed with MeCN and Et_2O. Metal content was determined by use of atomic absorption.[11] [CuCl(**2**)]: 66.4% yield. Calcd: Cu, 15.53. Found: Cu, 15.22. [CuBr(**2**)] (**12**): 85.3% yield. Calcd: Cu, 14.01. Found: Cu, 14.07. [CuI(**2**)]: 74.7% yield. Calcd: Cu, 12.69. Found: Cu, 11.98. [$(CuI)_2$(**2**)]: 64.7% yield. Calcd: Cu, 18.39. Found: Cu, 18.28. X-ray quality crystals of **12** were grown by heating a suspension in MeCN for 4 days in a sealed, evacuated glass tube at 100 °C.

Nickel(0) Complexes. [Ni$(P(OPh)_3)_4$] (0.650 g, 0.505 mmol) and **2** (0.250 or 0.500 mmol) or **10** (0.167 mmol) were suspended in 10 mL of MeCN and stirred at room temperature over 6 days. The resulting white precipitate was collected by filtration and washed with MeCN and Et_2O. [Ni$(P(OPh)_3)_2$-(**2**)]: 84.3% yield. Anal. Calcd for $C_{46}H_{46}NiO_{13}P_4$: C, 55.84; H, 4.69. Found: C, 55.86; H, 4.77. [Ni$(P(OPh)_3)_3$$(\mathbf{2})_{1/2}$]: 84.8% yield. Anal. Calcd for $C_{59}H_{53}NiO_{12.5}P_4$: C, 61.91; H, 4.67. Found: C, 61.87; H, 4.67. [Ni$(P(OPh)_3)_3$$(\mathbf{10})_{1/3}$]: 73.8% yield. Anal. Calcd for $C_{62}H_{54}NiO_{14}P_4$: C, 61.76; H, 4.51. Found: C, 61.82; H, 4.52.

X-ray Diffraction. Data for **7** and **11** were collected at 293(2) K and **12** at 153(2) K on a Mercury CCD area detector coupled with a Rigaku AFC-8S diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected and processed using Crystal Clear. The structure was solved by direct methods. Least-squares refinement of F^2 used all reflections. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by standard difference Fourier techniques and were refined with isotropic thermal parameters. Structure solution, refinement, and the calculation of derived results were performed using the SHELXTL package of computer programs.

Acknowledgment. We gratefully acknowledge support from the Henry Dreyfus Teacher-Scholar Awards Program of the Camille and Henry Dreyfus Foundation (TH-99-010) and from the Thomas F. and Kate Miller Jeffress Memorial Trust (J-678). This research was also supported in part by a Howard Hughes Medical Institute grant through the Undergraduate Biological Sciences Education Program to the College of William and Mary (M.E.D., A.B.W., and J.R.C.) and by a Beckman Scholarship from the Arnold and Mabel Beckman Foundation (M.E.D.). We also acknowledge the College of William & Mary for a faculty semester research assignment (R.D.P.). Financial support of the National Science Foundation for purchase of the CCD-based X-ray system at Clemson (CHE-9808165) is gratefully acknowledged.

Supporting Information Available: ^1H and ^{13}C NMR spectra of **1**−**11**. Crystallographic data for **7**, **11**, and **12**: CIF and tables of atomic coordinates and equivalent isotropic displacement coefficients, bond lengths and angles, and anisotropic displacement coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049957R

---

[11] Graham, P. M.; Pike, R. D.; Sabat, M.; Bailey, R. D.; Pennington, W. T. *Inorg. Chem.* **2000**, *39*, 5121.

[12] Maeyer, J. T.; Johnson, T. J.; Smith, A. K.; Borne, B. D.; Pike, R. D.; Pennington, W. T.; Krawiec, M.; Rheingold, A. L. *Polyhedron* **2003**, *22*, 419.