McMurry Coupling of 2-Acylphosphacymantrenes: *E*- vs *Z*-Stereochemistry of the 1,2-Bis(phosphacymantrenyl) Alkenes

Patrick Toullec, Louis Ricard, and François Mathey*

Laboratoire "Hétéroéléments et Coordination", UMR CNRS 7653, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

Received February 20, 2002

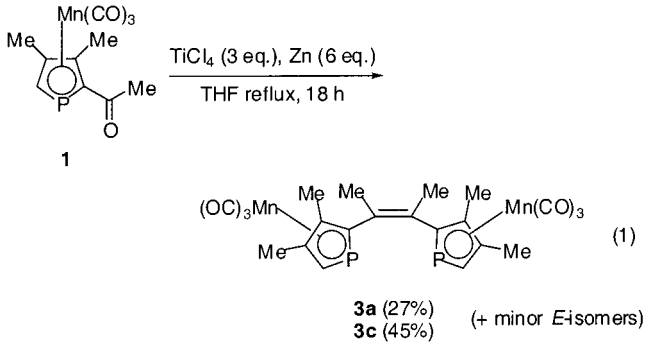
The McMurry coupling of a 2-acetylphosphacymantrene with the $TiCl_4$/Zn couple preferentially provides the *Z*-alkene as a mixture of the *rac* and *meso* diastereomers. The coupling of the 2-benzoylphosphacymantrene mainly gives the *E*-alkene together with the 2-benzyl reduction product. The alkene stereochemistries have been established by X-ray crystal structure analyses. A titanium−carbene intermediate is suggested in the second case.

Introduction

A lot of work has been devoted to the synthesis of hetero analogues of porphyrins.[1] However, the phosphorus analogues remain conspicuous by their absence. There are at least two difficulties that hamper the synthesis of phosphaporphyrins. The first one is purely structural. The C−P−C intracyclic angle in a phosphole unit typically lies around 90°,[2] whereas the corresponding C−N−C angle in a pyrrole unit is less acute at ca. 110°. Besides, the covalent radius of phosphorus is substantially larger than the covalent radius of nitrogen: 1.10 vs 0.70 Å. As a consequence, the exact P-analogue of a porphyrin probably does not exist, the central hole being insufficient to accommodate the bigger P atoms and the more acute ∠CPC angles of the phosphole units. The second difficulty lies in the lack of aromatic character of the phosphole ring,[3] which prevents the use of the classical functionalization techniques that are employed in most of the routes to porphyrins. Since the structural features of the phosphole ring suggest that monatomic linkers such as the sp^2-C units of porphyrins are inappropriate for the synthesis of phosphaporphyrins, it is logical to investigate the use of the larger 1,2-alkenediyl units.[4] Thus we were led to investigate possible routes to *Z*-1,2-bis(2-phospholyl)alkenes. The McMurry coupling[5] of 2-acylphosphole derivatives was an obvious choice. A preliminary report on the coupling of 2-formylphospholes stated that the resulting alkenes essentially display the *E*-stereochemistry,[6] so we decided to investigate the McMurry coupling of the easily accessible 2-acylphosphacymantrenes in which the absence of P-substituents might favor the *Z*-stereochemistry.[7]

Results and Discussion

Our starting products were the readily available 2-acetyl (**1**) and 2-benzoyl (**2**) derivatives.[8] The coupling of the 2-acetylphosphacymantrene **1** was carried out in refluxing THF with a $TiCl_4$/Zn couple (eq 1).



The formation of the four expected isomers (*meso*, *rac*; *Z*, *E*) was monitored by ^{31}P NMR of the crude reaction mixture after removal of the inorganic byproducts: **3a**: δ ^{31}P −22.2 (major); **3b**: δ ^{31}P −26.1 (minor); **3c**: δ ^{31}P −28.2 (major); **3d**: δ ^{31}P −28.4 (minor). The two major isomers were recovered as pure products by chromatography. The first eluted species was **3c**, isolated in 45% yield. In the mass spectrum (EI, 70 eV), a small molecular peak appears at *m*/*z* 552, and the base peak at *m*/*z* 329 corresponds to the loss of 6 CO and 1 Mn.

(1) Latos-Grazynski, L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. H., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 2, pp 361−416.
(2) Phosphole, C. P.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1973**, 1888. Phospholide, D. T.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1367.
(3) Quin, L. D. In *Phosphorus−Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F., Ed.; Pergamon: Oxford, 2001; pp 219−362. Mathey, F. *Chem. Rev.* **1988**, *88*, 429.
(4) Expanded tetraoxaporphyrins with 1,2-ethenediyl linkers have been recently described: Vogel, E.; Jux, N.; Dörr, J.; Pelster, T.; Berg, T.; Böhm, H.-T.; Lex, J.; Bremm, D.; Hohlneicher, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1101.
(5) Reviews: McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513. Fürstner, A.; Bogdanovic, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2442.
(6) Niemi, T.-A.; Coe, P. L.; Till, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1519.
(7) The McMurry coupling of 2-acetylcymantrene is known to give predominantly the *Z*-alkene, see: Pitter, S.; Huttner, G.; Walter, O.; Zsolnai, L. *J. Organomet. Chem.* **1993**, *454*, 183. See also: Top, S.; Kaloun, E. B.; Toppi, S.; Herrbach, A.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **2001**, *20*, 4554.
(8) Mathey, F. *Tetrahedron Lett.* **1976**, 4155. Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 5748.

10.1021/om020144h CCC: $22.00
Publication on Web 05/30/2002

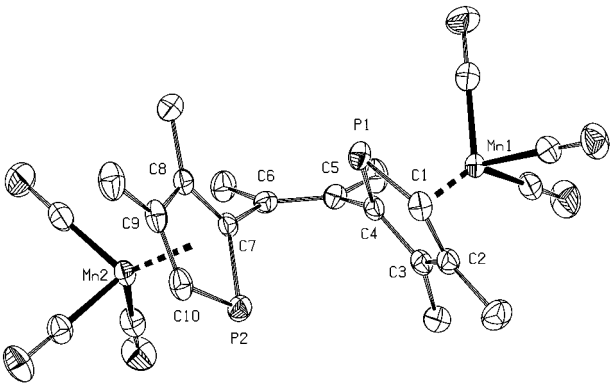


Figure 1. ORTEP drawing of one molecule of **3c**. Selected bond distances (Å) and angles (deg): Mn(1)−P(1) 2.3845(8), P(1)−C(1) 1.757(2), P(1)−C(4) 1.787(2), C(1)−C(2) 1.409(3), C(2)−C(3) 1.430(3), C(3)−C(4) 1.417(3), C(4)−C(5) 1.491(3), C(5)−C(6) 1.345(3), C(6)−C(7) 1.493(3); C(1)−P(1)−C(4) 89.0(1), C(4)−C(5)−C(6) 119.7(2), C(5)−C(6)−C(7) 120.3(2).

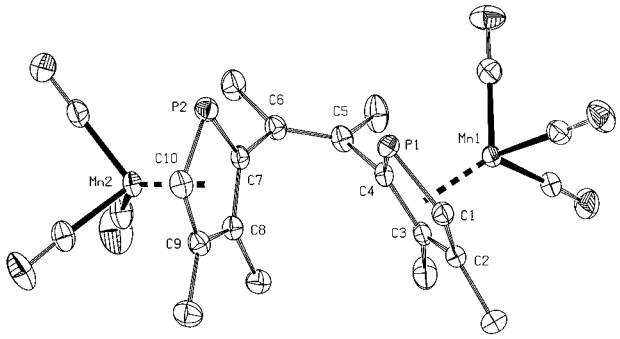
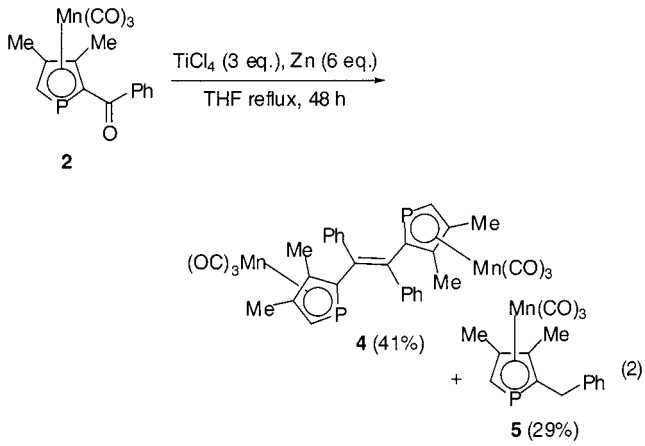


Figure 2. ORTEP drawing of one molecule of **3a**. Selected bond distances (Å) and angles (deg): Mn(1)−P(1) 2.3859(8), P(1)−C(1) 1.763(2), P(1)−C(4) 1.795(2), C(1)−C(2) 1.402(3), C(2)−C(3) 1.438(2), C(3)−C(4) 1.422(2), C(4)−C(5) 1.491(2), C(5)−C(6) 1.346(2), C(6)−C(7) 1.490(2); C(1)−P(1)−C(4) 88.75(8), C(4)−C(5)−C(6) 120.8(2), C(5)−C(6)−C(7) 121.2 (1).

The ^{13}C NMR spectrum shows the sp^2-carbons of the bridge as a pseudotriplet at 131.48 with $\sum J_{CP} = 16.5$ Hz. The stereochemistry was established by X-ray crystal structure analysis (Figure 1). The C═C bridge displays the desired *Z*-stereochemistry. The two phosphacymantrene rings lie almost parallel in a head-to-tail disposition corresponding to the *rac*-diastereomer with the two $Mn(CO)_3$ moieties oriented away from each other in order to minimize steric crowding. The C═C double bond is well localized at 1.345(3) Å and shows no distortion with all the C−C═C angles close to 120°. The second major isomer, **3a**, displays spectral characteristics similar to **3c**. In particular, the carbons of the bridge appear as a pseudotriplet at 130.76 with $\sum J_{CP} =$ 18 Hz. Once again, the stereochemistry was established by X-ray crystal structure analysis (Figure 2). The C═C bridge displays the *Z*-stereochemistry; the two phosphacymantrene rings are approximately parallel with a head-to-head disposition corresponding to the *meso*-diastereomer. The structural parameters are very similar to those of **3c**.

The findings were entirely different with the 2-benzoylphosphacymantrene **2**. Under similar reaction conditions but a longer reaction time, the reaction led to a major coupled isomer **4** plus a reduction product **5** (eq 2).



The mass spectrum of **4** (EI) displays a small (M + 2) peak at *m*/*z* 678 and a base peak at *m*/*z* 454 corresponding to the loss of 6 CO and 1 Mn. In the ^{13}C spectrum, the carbons of the bridge appear as a multiplet at 140.20. The X-ray crystal structure analysis (Figure 3) demonstrates that **4** displays a center of symmetry and a *E*-stereochemistry. No distortion of the C═C bond of the bridge is visible. The structure of the reduction product **5** was deduced from mass and ^{1}H and ^{13}C NMR spectroscopy. The formation of the reduction product and the change of stereochemistry suggest a change of mechanism in the McMurry coupling of the benzoyl derivative **2** when compared to **1**. In line with recent proposals on the coupling mechanism of hindered ketones,[9] we suggest a titanium−carbene intermediate (Ti═C) whose hydrolysis would rationalize the formation of **5**. The reasons behind the change of stereochemistry are less clear, but it must be recalled that the preferential *Z*-stereochemistry of the coupling products derived from **1** is consistent with those observed in the coupling of acetylcymantrenes.[7] Finally, it must be

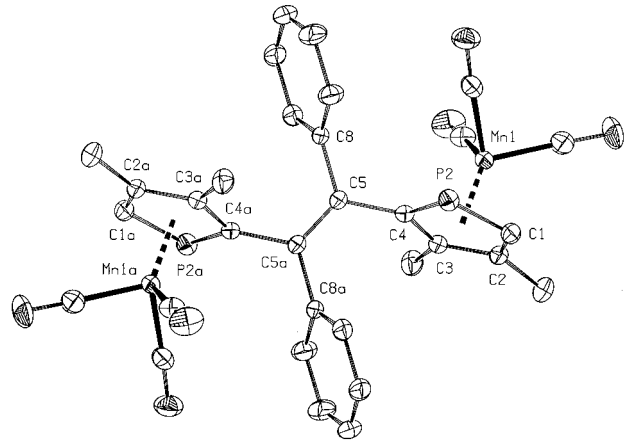


Figure 3. ORTEP drawing of one molecule of **4**. Selected bond distances (Å) and angles (deg): Mn(1)−P(2) 2.3745(6), P(2)−C(1) 1.758(2), P(2)−C(4) 1.787(2), C(1)−C(2) 1.406(3), C(2)−C(3) 1.425(2), C(3)−C(4) 1.424(2), C(4)−C(5) 1.497(2), C(5)−C(5a) 1.352(3); C(1)−P(2)−C(4) 88.90(8), C(4)−C(5)−C(5a) 120.3(2).

(9) Villiers, C.; Ephritikhine, M. *Chem. Eur. J.* **2001**, *7*, 3043.

stressed that efficient decomplexation techniques are available for the conversion of phosphacymantrenes into phospholes,[10] thus providing a solution to the synthetic problems outlined in the Introduction. However, as stated by one of the referees,[11] the X-ray data of **3a** and **3c** suggest that, in a coplanar conformation, the two phosphorus atoms of a *Z*-1,2-bis(phospholyl)alkene unit would be only about 1.43 Å apart. This is too close for accommodating a metal. Thus probably, other linkers than the *Z*-1,2-alkenediyl are still to be found for the successful synthesis of phosphaporphyrins.

Experimental Section

General Considerations. All reactions were performed under an inert atmosphere with dry, deoxygenated solvents by using vacuum line and Schlenk tube techniques. 2-Acetyl-3,4-dimethylphosphacymantrene and 2-benzoyl-3,4-dimethylphosphacymantrene were prepared according to known procedures.[8] All other reagents are commercial grade and used as received. NMR spectra were measured on a Bruker 300 MHz multinuclear spectrometer. Chemical shifts are expressed in ppm from internal TMS (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P); couplings constants are expressed in Hz. Mass spectra (electron impact) were measured at 70 eV by the direct inlet method. Elemental analyses were performed at the Service de Microanalyse du CNRS, Gif-sur-Yvette, France.

McMurry Coupling of 2-Acetyl-3,4-dimethylphosphacymantrene. A 1.57 g sample of zinc dust (24 mmol) was placed in a 150 mL Schlenk tube under nitrogen atmosphere, and 50 mL of distilled THF was added. The Schlenk tube was cooled to 0 °C, and 1.3 mL of titanium tetrachloride (12 mmol) was added slowly. The resulting solution was refluxed for 2 h, then 1.16 g (4 mmol) of 2-acetyl-3,4-dimethylphosphacymantrene dissolved in 20 mL of distilled THF was added. The solution was refluxed for 18 h. The solvents were removed under reduced pressure, and the crude mixture was redissolved in 70 mL of diethyl ether. The solution was treated with 2 × 50 mL of saturated sodium hydrogen carbonate aqueous solution and washed with 50 mL of water. The organic layer was collected, dried with magnesium sulfate, and filtered, and the solvents were removed under vacuum to give 1.03 g of a yellow crystalline solid as a mixture of the four isomers of the final products. Chromatography over silica gel with a 97:3 hexane/ether mixture as the eluent was carried out, yielding 490 mg of **3c** first, then 300 mg of **3a**. Total yield of the two *Z*-isomers: 72.5%.

***rac*-(*Z*)-2,3-Bis[3′,4′-dimethylphosphacymantren-2′-yl]-but-2-ene (3c).** ^{31}P{^{1}H} NMR (CH_2Cl_2): δ −28.2. ^{1}H NMR ($CDCl_3$): δ 1.82 (s, 6H, ethylenic CH_3); 2.10 (s, 6H, CH_3−C$^{4'}$); 2.17 (s, 6H, CH_3−C$^{3'}$); 4.67 (dm, J = 34.5 Hz; 2H). ^{3}C NMR ($CDCl_3$): δ 13.77 (s, *C*H_3−C$^{4'}$); 16.57 (s, *C*H_3−C$^{3'}$); 26.16 (s, ethylenic CH_3); 92.25 (dm, J = 68.7 Hz, C$^{5'}$); 106.87 (s, C$^{4'}$); 116.45 (s, C$^{3'}$); 121.37 (dm, J = 52.8 Hz, C$^{2'}$); 131.48 (pseudotriplet, J = 16.5 Hz; ethylenic carbon); 224.92 (s, CO). MS: *m*/*z* 552 (M^+, 1%); 524 (M^+ − CO, 16%); 468 (M^+ − 3CO, 18%); 440 (M^+ − 4CO, 13%); 384 (M^+ − 6CO, 75%); 329 (M^+ − 6CO − Mn, 100%). Anal. Calcd for $C_{22}H_{20}O_6P_2Mn_2$: C, 47.83; H, 3.62. Found: C, 47.29; H, 3.91.

***meso*-(*Z*)-2,3-Bis[3′,4′-dimethylphosphacymantren-2′-yl]but-2-ene (3a).** ^{31}P{^{1}H} NMR (CH_2Cl_2): δ −22.2. ^{1}H NMR ($CDCl_3$): δ 1.78 (s, 6H); 1.79 (s, 6H); 2.06 (s, 6H, ethylenic CH_3); 4.46 (dm, J = 35.0 Hz, 2H). ^{3}C NMR ($CDCl_3$): δ 14.57 (s, *C*H_3−C$^{4'}$); 16.46 (s, *C*H_3−C$^{3'}$); 27.27 (s, ethylenic CH_3); 95.95 (dm, J = 64.1 Hz, C$^{5'}$); 108.74 (s, C$^{4'}$); 114.04 (s, C$^{3'}$); 121.89 (dm, J = 57.4 Hz, C$^{2'}$); 130.76 (pseudotriplet, J = 18.2 Hz, ethylenic carbon); 224.66 (s, CO). MS: *m*/*z* 524 (M^+ − CO, 12%); 468 (M^+ − 3CO, 18%); 440 (M^+ − 4CO, 3%); 384 (M^+ − 6CO, 52%); 329 (M^+ − 6CO − Mn, 100%). Anal. Calcd for $C_{22}H_{20}O_6P_2Mn_2$: C, 47.83; H, 3.62. Found: C, 47.41; H, 3.94.

McMurry Coupling of 2-Benzoyl-3,4-dimethylphosphacymantrene. A 1.17 g sample of zinc dust (18 mmol) was placed in a 150 mL Schlenk tube under nitrogen atmosphere, and 50 mL of distilled THF was added. The Schlenk tube was cooled to 0 °C, and 1 mL of titanium tetrachloride (9 mmol) was added slowly. The resulting solution was refluxed for 2 h, then 0.9 g (2.55 mmol) of 2-acetyl-3,4-dimethylphosphacymantrene dissolved in 20 mL of distilled THF was added. The solution was refluxed for 48 h. The solvents were removed under reduced pressure, and the crude mixture was redissolved in 50 mL of diethyl ether. The solution was treated with 2 × 50 mL of saturated sodium hydrogen carbonate aqueous solution and washed with 50 mL of water. The organic layer was collected, dried with magnesium sulfate, and filtered, and the solvents were removed under vacuum to give an orange oil that partly crystallized. Chromatography over silica gel with a 97:3 hexane/ether mixture as the eluant first gave 250 mg of **5**, then 350 mg of **4**.

2-Benzyl-3,4-dimethylphosphacymantrene (5). ^{31}P{^{1}H} NMR (CH_2Cl_2): δ −38.6. ^{1}H NMR ($CDCl_3$): δ 2.06 (s, 3H); 2.14 (s, 3H); 3.39 (d, J = 1.6 Hz, 1H); 3.44 (s, 1H); 4.30 (d, J = 35 Hz, 1H); 7.2−7.3 (m, 5H). ^{3}C NMR ($CDCl_3$): δ 13.30 (s); 16.55 (s); 36.10 (d, J = 18.9 Hz, CH_2); 94.07 (d, J = 58.9 Hz, C$^{5'}$); 110.00 (d, J = 6.8 Hz, C$^{4'}$); 113.51 (d, J = 7.5 Hz, C$^{3'}$); 120.71 (d, J = 60.4 Hz, C$^{2'}$); 127.32 (s, C_{para}); 129.12 (s, C_{ortho}); 129.27 (s, C_{meta}); 140.50 (d, J = 1.5 Hz, C_{ipso}); 224.87 (s, CO). MS: *m*/*z* 339 (M^+ − 1, 9%); 283 (M^+ − 1 − 2CO, 4%); 255 (M^+ − 1 − 3CO, 100%); 201 (M^+ − 3CO − Mn, 14%).

***rac*-(*E*)-1,2-Bis[3′,4′-dimethylphosphacymantren-2′-yl]-1,2-diphenylethene (4).** ^{31}P{^{1}H} NMR (CH_2Cl_2): δ −19.3. ^{1}H NMR ($CDCl_3$): δ 1.89 (s, 12H); 4.13 (d, J = 35.4 Hz, 2H); 7.05−7.25 (m, 10H). ^{3}C NMR ($CDCl_3$): δ 15.05 (s); 16.18 (s); 93.80 (d, J = 63.4 Hz, C$^{5'}$); 108.05 (d, J = 6.8 Hz, C$^{4'}$); 115.00 (d, J = 3 Hz, C$^{3'}$); 119.14 (d, J = 57.4 Hz, C$^{2'}$); 127.78 (s, C_{ortho}); 128.45 (s, C_{meta}); 130.25 (s, C_{para}); 140.20 (m, ethylenic carbon); 144.62 (s, C_{ipso}); 224.12 (s, CO). MS: *m*/*z* 678 (M^+ + 2H, 2%); 650 (M^+ + 2H − CO, 10%); 592 (M^+ − 3CO, 70%); 509 (M^+ − 6CO + H, 55%); 454 (M^+ − 6CO − Mn, 100%). Anal. Calcd for $C_{32}H_{24}O_6P_2Mn_2$: C, 56.80; H, 3.55. Found: C, 56.68; H, 3.77.

X-ray Crystal Structures. All data were collected on a KappaCCD diffractometer at 150.0(1) K with Mo Kα radiation (λ = 0.71073 Å). Full details of the crystallographic analysis are described in the Supporting Information.

Crystallographic data for $C_{22}H_{20}Mn_2O_6P_2$, **3a**: M = 552.20 g/mol; triclinic; space group $P\bar{1}$; a = 7.558(5) Å, b = 12.384(5) Å, c = 13.786(5) Å, α = 108.110(5)°, β = 98.760(5)°, γ = 104.430(5)°, V = 1150.1(10) Å^3; Z = 2; D = 1.595 g cm^{-3}; μ = 1.273 cm^{-1}; F(000) = 560. Crystal dimensions 0.20 × 0.14 × 0.10 mm. Total reflections collected 9356 and 5650 with $I > 2\sigma(I)$. Goodness of fit on F^2 1.018; $R(I > 2\sigma(I))$ = 0.0326, wR2 = 0.0914 (all data); maximum/minimum residual density 0.927(0.068)/−0.525(0.068) e Å^{-3}.

Crystallographic data for $C_{22}H_{20}Mn_2O_6P_2$, **3c**: M = 552.20 g/mol; monoclinic; space group $P2_1/n$; a = 7.946(5) Å, b = 12.668(5) Å, c = 23.622(5) Å, β = 92.610(5)°, V = 2375.3(18) Å^3; Z = 4; D = 1.544 g cm^{-3}; μ = 1.233 cm^{-1}; F(000) = 1120. Crystal dimensions 0.20 × 0.20 × 0.20 mm. Total reflections collected 16 064 and 6196 with $I > 2\sigma(I)$. Goodness of fit on F^2 1.032; $R(I > 2\sigma(I))$ = 0.0255, wR2 = 0.0733 (all data); maximum/minimum residual density 0.400(0.074)/−0.456(0.074) e Å^{-3}.

Crystallographic data for $C_{32}H_{24}Mn_2O_6P_2$, **4**: M = 676.33 g/mol; monoclinic; space group $P2_1/n$; a = 11.1367(2) Å, b = 12.6396(4) Å, c = 11.4394(3) Å, β = 114.2360(10)°, V = 1468.32(7) Å^3; Z = 2; D = 1.530 g cm^{-3}; μ = 1.013 cm^{-1}; F(000) = 688. Crystal dimensions 0.16 × 0.16 × 0.16 mm. Total reflections collected 7036 and 3272 with $I > 2\sigma(I)$. Goodness of fit on F^2

(10) Deschamps, B.; Toullec, P.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **2001**, *634*, 131.

(11) We are grateful to Prof. Michael McGlinchey for this remark.

1.059; $R(I > 2\sigma(I)) = 0.0384$, wR2 = 0.1063 (all data); maximum/minimum residual density 0.980(0.077)/−0.519(0.077) e Å^{-3}.

Acknowledgment. The authors thank BASF for the financial support of Patrick Toullec and of this research program.

Supporting Information Available: Listings of atomic coordinates, including equivalent isotropic displacement parameters, bond lengths, and bond angles of **3a**, **3c**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020144H