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An access to original 3,3-bis(phospholyl)lactones

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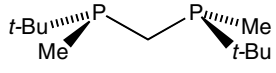
Abstract

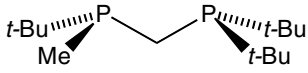
The reaction of lithium 3,4-dimethylphospholide with dicarboxylic acid dichlorides yields the original 3,3-bis(3,4-dimethylphospholyl)lactones via an unexpected cyclization reaction. One of the products has been characterized by X-ray crystal structure analysis of its bis(pentacarbonylmolybdenum) complex.

1. Introduction

Recently, the interest in 1,1-bis(phosphino)alkanes has raised considerably due to the discovery that some of them, such as MiniPHOS **1** [1] and its monochiral analogue **2**, [2] are extremely efficient ligands in enantioselective catalysis.



MiniPHOS (**1**)

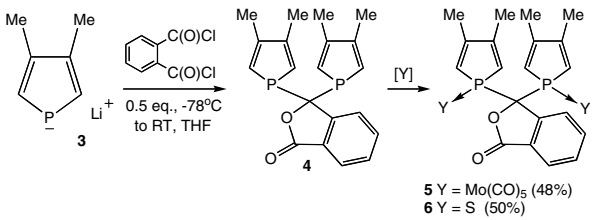


(**2**)

The P–CH_2–P link is generally built via the reaction of the borane complex of a phosphinomethyl carbanion with a dichlorophosphine.

From another standpoint, phospholes have proven their worth in the rhodium-catalyzed hydroformylation of olefins [3] and in the palladium-catalyzed copolymerization of ethylene and carbon monoxide. [4] These considerations suggest that 1,1-bis(phospholyl)alkanes are potentially very interesting ligands for transition metal-catalyzed reactions. In such a context, the discovery of a quite original route to the still unknown 3,3-bis(phospholyl)lactones deserves attention.

Some time ago, we started a systematic investigation of the reaction of acyl chlorides with phospholide ions. The initial reaction takes place at phosphorus but the 1-acylphospholes thus obtained are quite unstable because the acyl group tends to migrate from phosphorus to the α-carbons of the ring at low temperature [5]. As a logical extension of this initial study, we decided to investigate the reaction of phospholide ions with diacyl dichlorides. The first experiment was carried out with lithium 3,4-dimethylphospholide **3** and phthaloyl dichloride. To our surprise, we did not observe the expected shift but the formation of the stable lactone **4** (Eq. (1)).



(1)

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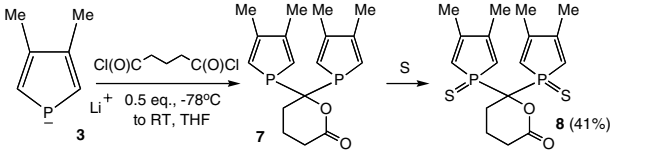
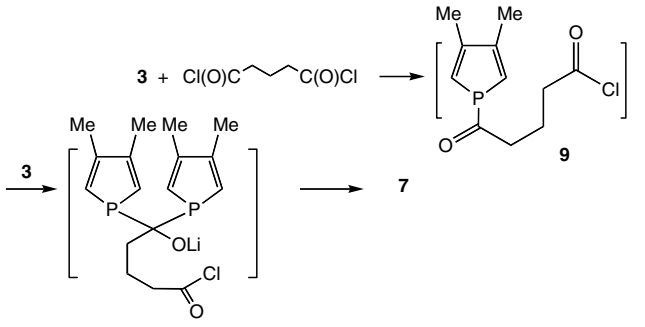
The reaction is very clean and appears almost quantitative [δ^{31}P(**4**) 12.7 ppm in THF]. The lactone has been transformed into its bis-($Mo(CO)_5$) complex **5** and its bis-sulfide **6** for complete characterization. The structure has been established by X-ray analysis of the molybdenum complex (Fig. 1). The phosphole rings show no special distortion, the P–C–P angle is rather wide at 116.13(14)°.

We then attempted to generalize this reaction in two directions. We first checked that other diacyl dichlorides could be used. The same type of transformation can indeed be performed with glutaryl dichloride (Eq. (2)).



(2)

Once again, the reaction is very clean and appears almost quantitative [δ^{31}P(**7**) 17.0 ppm in THF]. The lactone has been transformed into its its bis-sulfide **8** for complete characterization. We were less successful when trying to replace the phospholide ion by a more classical phosphide. All our attempts with lithium diphenylphosphide gave complex mixtures of products. The proposed mechanism is depicted in Eq. (3):



(3)

The surprising fact is that the second molecule of phospholide **3** selectively attacks the phospholyl-C(O) group of **9** rather than the acyl chloride. This reaction is extremely fast since it takes place before the quite easy [1,5]-shift of the acyl group around the phosphole ring can occur. We cannot rationalize these findings at the moment. The different behaviors of **3** and lithium diphenylphosphide is probably related to their quite different nucleophilicities. Indeed, phospholides are known to be much less basic than phosphides as a result of their strong aromatic stabilization energy [6]. From another standpoint, it is quite clear that numerous tridentate ligands can be obtained from **4** and **7** by taking advantage of the chemistry of lactones.

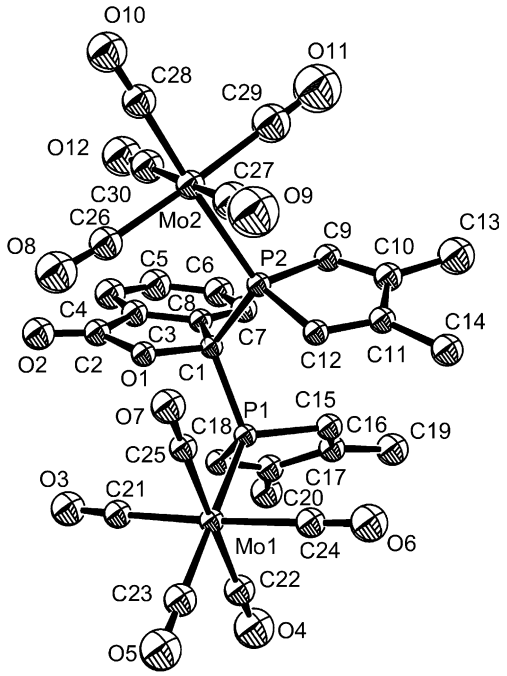


Fig. 1. ORTEP drawing of **5**. Significant bond distances (Å) and angles (°): P(1)–Mo(1) 2.4934(8), P(2)–Mo(2) 2.5296(9), P(1)–C(1) 1.895(3), P(2)–C(1) 1.895(3), P(1)–C(15) 1.795(3), P(1)–C(18) 1.798(3), P(2)–C(9) 1.787(3), P(2)–C(12) 1.793(3), C(1)–O(1) 1.457(3), O(1)–C(2) 1.386(4), C(2)–O(2) 1.194(4), C(2)–C(3) 1.462(5), C(3)–C(8) 1.377(4), C(8)–C(1) 1.506(4); P(1)–C(1)–P(2) 116.18(14), C(15)–P(1)–C(18) 90.90(16), C(15)–P(1)–C(1) 105.32(14), C(18)–P(1)–C(1) 103.21(14), C(9)–P(2)–C(12) 90.93(15), C(9)–P(2)–C(1) 105.12(14), C(12)–P(2)–C(1) 108.12(13), P(1)–C(1)–C(8) 112.0(2), P(2)–C(1)–C(8) 112.3(2), O(1)–C(1)–C(8) 104.0(2), C(1)–O(1)–C(2) 110.8(2), O(1)–C(2)–O(2) 120.9(3), O(1)–C(2)–C(3) 107.3(3).

2. Experimental

Reactions were performed under nitrogen using oven-dried glassware. Dry tetrahydrofuran was obtained by distillation from Na/benzophenone. Silica gel (70–230 mesh) was used for chromatographic separation. Nuclear magnetic resonance spectra were obtained on a Bruker Avance 3000 and Varian Inova spectrometer operating at 300.13 MHz for ^{1}H, 75.45 MHz for ^{13}C, and 121.496 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P) and data are reported as follows: chemical shift, multiplicity(s, singlet; d, doublet; t, triplet; m, multiplet; b, broad), integration, and coupling constants in hertz. Mass spectra were obtained on VG 7070 and Hewlett–Packard 5989A GC/MS spectrometers. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, Az. Starting materials were obtained from commercial suppliers or prepared according to literature methods.

2.1. Synthesis of complex 5

To a solution of 1-phenyl-3,4-dimethylphosphole (2 g, 10.6×10^{-3} mol) in 40 mL of dry THF was added 0.18 g (26×10^{-3} mol) of Li wire. After overnight stirring, the excess of lithium was removed; ^{t}BuCl (1.17 mL, 10.6×10^{-3} mol) was added and the reaction mixture stirred at 60 °C for 0.5 h. The THF solution of **3** was cooled down to −78 °C, phthaloyl dichloride (0.77 mL, 5.3×10^{-3} mol) was rapidly added and the system warmed to room temperature in 1 h. [$Mo(CO)_5CH_3CN$] (10.6×10^{-3} mol) in 28 mL CH_3CN was added. After stirring at 50 °C for 3 h, the solvent was distilled; the residue was chromatographed on silica gel with a mixture of hexane and successively 10%, 20%, 30% and 100% of dichloromethane. Vacuum distillation of the solvent gave a grey green powder: yield 2.1 g (48%).

^{31}P NMR ($CDCl_3$): δ 56.3; ^{1}H NMR ($CDCl_3$): δ 2.11 (dd, 12H, $^{4}J_{H-H}$ = 2.8 Hz, $^{4}J_{H-P}$ = 11.0 Hz, Me), 6.06 (d, 2H, $^{2}J_{H-P}$ = 34.0 Hz, CH–P), 6.18 (d, 2H, $^{2}J_{H-P}$ = 36.0 Hz, CH–P), 7.46, 7.62, 7.72, 7.94 (4 × m, 4H, H benzo); ^{13}C NMR ($CDCl_3$): δ 17.12 (pseudo-t, Me), 17.71 (pseudo-t, Me), 86.10 (t, CP_2), 148.00 (s, *ipso*-C(CP_2)), 151.92 (pseudo-t, C–Me), 152.66 (pseudo-t, C–Me), 168.33 (s, CO), 204.41 (*cis*-CO), 208.71 (*trans*-CO). Anal. Calc. for $C_{30}H_{20}Mo_2O_{12}P_2$: C, 43.61; H, 2.44. Found: C, 43.70; H, 2.66%.

2.2. Synthesis of sulfide 6

The THF solution of **3** was cooled down to −78 °C, phthaloyl dichloride (0.77 mL, 5.3×10^{-3} mol) was rapidly added and the system warmed to room temperature in 1 h. Then sulfur (0.68 g, 21×10^{-3} mol) was added and the resulting reaction mixture was stirred at 50 °C for 3 h. The solvent was distilled; the residue was chromatographed on silica gel with hexane and then ethyl acetate successively. Vacuum distillation of the solvent gave an orange powder: yield 1.2 g (50%).

^{31}P NMR ($CDCl_3$): δ 58.7; ^{1}H NMR ($CDCl_3$): δ 1.87 (s, 6H, Me), 1.95 (s, 6H, Me), 5.76 (m, 2H, CH–P), 6.23 (m, 2H, CH–P), 7.59 (m, 2H, H benzo), 7.82, 7.99 (2 × m, 2H, H benzo); ^{13}C NMR ($CDCl_3$): δ17.18 (pseudo-t, Me), 89.00 (t, $^{1}J_{C-P}$ = 47.1 Hz, CP_2), 144.25 (s, *ipso*-C(CP_2)), 155.43 (pseudo-t, C–Me), 156.62 (pseudo-t, C–Me), 167.92 (s, CO). Mass spectrum (EI): *m*/*z* 418 (M^+, 12%).

2.3. Synthesis of sulfide 8

The THF solution of **1** was cooled down to −78 °C, glutaryl dichloride (0.68 mL, 5.3×10^{-3} mol) was rapidly added and the system warmed to room temperature in 1 h. Then sulfur (0.68 g, 21×10^{-3} mol) was added and the resulting reaction mixture was stirred at 50 °C for 3 h. The solvent was distilled; the residue was chromatographed on silica gel with a mixture of hexane and successively 10%, 100% ether and then ethyl acetate successively. Vacuum distillation of the solvent gave a white solid: yield 0.84 g (41%).

^{31}P NMR ($CDCl_3$): δ 64.0; ^{1}H NMR ($CDCl_3$): δ 2.02 (s, 12H, Me), 2.35 (m, 4H, CH_2), 4.02 (m, 2H, CH_2O), 6.03 (m, 2H, CH–P), 6.17 (m, 2H, CH–P); ^{13}C NMR ($CDCl_3$): δ17.85 (m, Me), 18.09 (s, CH_2), 24.20 (s, CH_2), 29.83 (s, CH_2), 87.40 (t, $^{1}J_{C-P}$ = 50.0 Hz, CP_2), 120.53–122.08 (m, CH–P), 155.55 (pseudo-t, C–Me), 156.28 (pseudo-t, C–Me), 167.87 (s, CO). Mass spectrum (EI): *m*/*z* 384 (M^+). Anal. Calc. for $C_{17}H_{22}O_2P_2S_2$: C, 53.11; H, 5.77. Found: C, 53.47; H, 6.02%.

2.4. Crystal structure determination of complex 5

The Bruker SMART-1000 [7a] X-ray diffraction instrument with Mo-radiation was used for data collection of compounds **5**. All data frames were collected using ω-scan mode (−0.3° ω-scan width, hemisphere of reflections) and integrated using Bruker SAINTPLUS software package [7b]. The intensity data were corrected for Lorentzian polarization and absorption corrections were performed using the SADABS program incorporated in the SAINTPLUS software package. The Bruker SHELXTL software package [7c] was used for direct methods of phase determination and structure refinement. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of were refined by means of a full matrix least-squares procedure on F^2. All H-atoms were included in the refinement in calculated positions riding on the carbons atoms to which they were attached. Drawing was performed using ORTEP32 software [8] with 50% of probability for the non-hydrogen atoms. **5**: $C_{30}H_{20}O_{12}P_2Mo_2$, M_r = 826.28, crystal size $0.39 \times 0.18 \times 0.05$ mm^3, monoclinic, space group $P2_1/n$, a = 11.0613(4), b = 15.4244(6), c = 20.4604(7) Å, β = 97.9290(10)°, V = 3454.3(2) Å^3, $\rho_{calc.}$ = 1.589 mg/m^3, $2\theta_{max}$ = 56.00°, Mo Kα (λ = 0.71073 Å), low temperature = 233(2) K, total reflections collected = 25723, independent reflections = 8330 (R_{int} = 0.0478, R_{sig} = 0.0505), 6029 (72.4%) reflections were greater than $2\sigma(I)$, index ranges, $14 \leqslant h \leqslant 11$, $-20 \leqslant k \leqslant 19$, $-27 \leqslant l \leqslant 25$, absorption coefficient μ = 0.876 mm^{-1}; max/min transmission = 0.9575 and 0.7262, 419 parameters were refined and converged at R_1 = 0.0361, wR_2 = 0.0795, with intensity $I > 2\sigma(I)$, the final difference map was 0.853/−0.486 e/Å^3.

Data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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References

[1] Y. Yamanoi, T. Imamoto, J. Org. Chem. 64 (1999) 2988.
[2] G. Hoge, H.-P. Wu, W.S. Kissel, D.A. Pflum, D.J. Greene, J. Bao, J. Am. Chem. Soc. 126 (2004) 5966.
[3] (a) C. Bergounhou, D. Neibecker, R. Réau, J. Chem. Soc., Chem. Commun. (1988) 1370;
(b) C. Bergounhou, D. Neibecker, R. Réau, Bull. Soc. Chim. Fr. 132 (1995) 815.
[4] S. Doherty, G.R. Eastham, R.P. Tooze, T.H. Scanlan, D. Williams, M.R.J. Elsegood, W. Clegg, Organometallics 18 (1999) 3558.
[5] P. Toullec, F. Mathey, Synlett (2001) 1977.
[6] L.S. Sunderlin, D. Panu, D.B. Puranik, A.J. Ashe III, R.R. Squires, Organometallics 13 (1994) 4732.
[7] (a) SMART Software Reference Manual, Version 5.054, Bruker Analytical X-ray System, Inc., Madison, WI 1997–1998;
(b) SAINTPLUS Software Reference Manual, Version 6.02A, Bruker Analytical X-ray System, Inc., Madison, WI 1997–1998;
(c) SHELXTL Software Reference Manual, Version 6.10, December 5th, 2000, Bruker Analytical X-ray System, Inc., Madison, WI.
[8] ORTEP 3 for Windows L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.