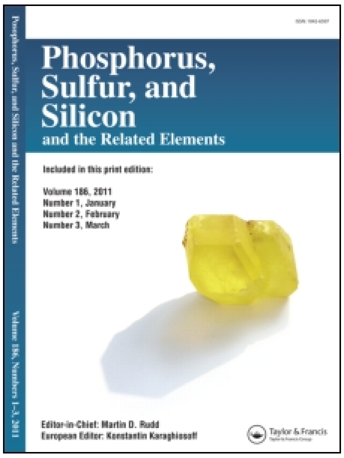


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

UNUSUAL TRIPOD-LIKE LIGANDS. SYNTHESIS OF 2,2-BIS(DIPHENYLPHOSPHINOMETHYL)-1-METHOXYPROPANE AND 2,2-BIS(PHENYLTHIOMETHYL)-1-METHOXYPROPANE

Shiuh-Tzung Liu[a]; Chien-Hung Yieh[a]; Hui-Jane Lu[a]
[a] Department of Chemistry, National Taiwan University, Taipei, Taiwan R.O.C.

To cite this Article Liu, Shiuh-Tzung , Yieh, Chien-Hung and Lu, Hui-Jane(1989) 'UNUSUAL TRIPOD-LIKE LIGANDS. SYNTHESIS OF 2,2-BIS(DIPHENYLPHOSPHINOMETHYL)-1-METHOXYPROPANE AND 2,2-BIS(PHENYLTHIOMETHYL)-1-METHOXYPROPANE', Phosphorus, Sulfur, and Silicon and the Related Elements, 44: 3, 261 — 265

To link to this Article: DOI: 10.1080/10426508908040617

URL: http://dx.doi.org/10.1080/10426508908040617

Phosphorus, Sulfur, and Silicon, 1989, Vol. 44, pp. 261–265
Reprints available directly from the publisher
Photocopying permitted by license only

UNUSUAL TRIPOD-LIKE LIGANDS. SYNTHESIS OF 2,2-BIS(DIPHENYLPHOSPHINOMETHYL)-1-METHOXYPROPANE AND 2,2-BIS(PHENYLTHIOMETHYL)-1-METHOXYPROPANE

SHIUH-TZUNG LIU,† CHIEN-HUNG YIEH and HUI-JANE LU
Department of Chemistry, National Taiwan University, Taipei,
Taiwan R.O.C. 10764

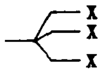
(Received November 3, 1988)

By employment of 1,1,1-tris(hydroxymethyl)ethane as the starting material, syntheses of two novel tripod-like terdentates with mixed donor properties, 2,2-Bis(diphenylphosphinomethyl)-1-methoxypropane (P_2O) and 2,2-Bis(diphenylphosphinomethyl)-1-methoxypropane (S_2O) are reported. Structural confirmation is based on spectroscopic and analytical results.

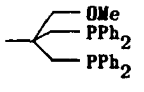
Key words: Tripodal ligands; terdentates; organophosphine ligand; organosulfur ligand.

INTRODUCTION

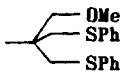
The coordination and organometallic chemistry associated with the tripodal terdentates have received attention recently.[1-5] Thus the triphos **1a** ligand has been shown to stabilize polyhydride rhodium(III) complexes[4] and sulfido metal complexes.[5] However, the tripodal ligands appeared in literatures are quite limited in the same donor atoms, such as all phosphorus atoms in **1a** or all sulfur atoms in **1b**; few are known as in mixed donor atoms.[6,7] The geometrical arrangement of tripodal ligands ideally provides themselves to occupy facial ligation sites in an octahedral complex. This feature would make tripod-like ligands with different donor properties useful to the study of transition metal coordination chemistry. Of particular interest to us have been the studies of new tripodal ligands with mixed donor atoms.[7] Syntheses of tripodal ligands, 2,2-Bis(diphenylphosphinomethyl)-1-methoxypropane (P_2O) and 2,2-Bis(phenylthiomethyl)-1-methoxypropane (S_2O) respectively, are presented in this paper.



1a X = PPh_2
1b X = SR



2



3

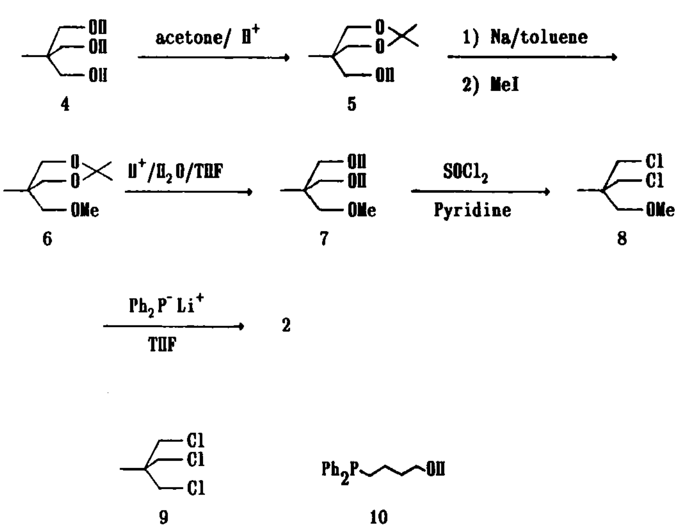
---

† Author to whom all correspondence should be addressed.

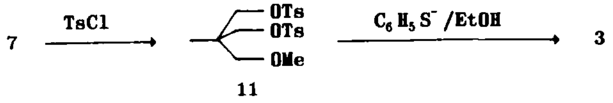
RESULTS AND DISCUSSION

Scheme I outlines the synthesis of **2**. By using 1,1,1-tris(hydroxymethyl)ethane **4** as starting material, two of the three hydroxy functions must be differentiated at some point during the synthesis. Thus triol **4** was converted into ketal alcohol **5** according to the literature procedure.[7] Metalation of **5** with sodium metal in refluxing toluene and subsequent treatment of methyl iodide to generate **6**, followed by the acidic hydrolysis gave diol **7** as clear, colorless liquid (60%). However, the conversion of alcohol **7** into the corresponding chloride seemed to be a critical step. Treatment of **7** with excess thionyl chloride and pyridine in chloroform under refluxing condition gave no desired product with recovery of starting material. While this reaction was carried out in the solvent of pyridine with heating at 115°C, the formation of trichloride **9** was observed, indicating the cleavage carbon–oxygen bond under this severe condition. Fortunately, the conversion of diol to its dichloride was best carried out by mixing **7** with excess thionyl chloride and 3.3 equivalent mole of pyridine at temperature ranging from 80–90°C for 4 hours. After a water workup, the desired dichloride **8** could be isolated in 58% yield. The chloride **8** was then treated with excess isolated in 58% yield. The chloride **8** was then treated with excess lithium diphenylphosphide, generated from the reductive cleavage of triphenylphosphine by lithium metal in THF, to produce **2**, accompanied with **10** as a side product. Anaerobic chromatography of the reaction mixture on degassed silica gel using hexane-ethyl acetate as eluent gave the desired tripodal phosphine ligand **2** as an air-sensitive, viscous oil in 64% yield. The formation of **10** was apparently resulted from the tetrahydrofuran ring-opening by the nucleophilic attack of diphenylphosphide anion.

The synthesis of **3** is shown scheme II. Unlike using **8** with chloride as leaving groups in the preparation of **2**, tosylate **11** was used for the substitution reaction.



SCHEME I



SCHEME II

In this way compound **7** was transformed into tosylate **11**, which reacted with thiophenolate anion in ethanol to afford **3** in 71% yield after chromatography on silica gel. This desired ligand was isolated as a clear, colorless liquid.

These two new tripodal ligands were all characterized by spectroscopic methods and elemental analysis. The ^1H NMR of **2** showed, besides aromatic and methyl absorptions, a doublet at 2.30 ppm with $J_{p-H} = 3$ Hz, which indicated the methylene unit attached to the diphenylphosphino sites; while the chemical shifts of the methylene and the methyl group adjacent to oxygen appear at 3.15 and 2.88 ppm respectively. The proton-decoupled ^{31}P NMR spectrum consisted of a singlet at −25.10 ppm. Additionally, the sp^3 hybridized carbon signals at 79.4 (t, $J_{P-C} = 8.3$ Hz), 57.7, 39.3 (dd, $J_{P-C} = 17.4$, 9.8 Hz), 38.6 (t, $J_{P-H} = 13.6$ Hz) and 25.0 (t, $J_{P-H} = 9.8$ Hz) were detected in the ^{13}C NMR spectrum of **2**. Thus all sp^3 hybridized carbons were splitted by two phohsphorus atoms, except methoxy carbon. This splitting patterns was another evidence to support the structure of **2**. The tripodal ligand **3** and other intermediates were easily confirmed by ^1H NMR spectroscopy (see experimental section).

In summary, we have developed an easy synthesis led to unusual tripodal ligands with mixed donor atoms. The synthesis of other donor atom systems and their coordination chemistry are currently under investigated.

EXPERIMENTAL

Proton magnetic resonance spectra are recorded on either a Varian EM-390 or a Brucker AM-300WB spectrometer. Carbon-13 and proton-decoupled phosphorous-31 NMR spectra are determined on a Brucker AM-300WB spectrometer at 75.48 and 121.49 MHz, respectively. Chemical shifts are given in parts per million relative to Me_4Si for ^{13}C and relative to 85% H_3PO_4 for ^{31}P NMR spectra in $CDCl_3$, unless otherwise noted. Chemical Shifts upfield of the standard defines as negative.

Infrared spectra are obtained on a Perkin–Elmer 1310 or 983G instrument. Mass spectra are determined on a Finnigan TSQ-46C instrument at 70 eV. Elemental analyses are carried out on a Perkin–Elmer 240C instrument. Melting points are determined on a Gallenkamp melting point apparatus and are uncorrected.

All of the reactions, manipulations, and purification steps involving phosphines are performed under a dry nitrogen or argon atmosphere. Air-sensitive liquids are transferred by Telfon flexneedles using nitrogen pressure or by syringe. All concentration of solutions are carried out on a rotary evaporator with water aspirator pressure. Solutions are dried with anhydrous, degassed magnesium sulfate.

Tetrahydrofuran and diethyl ether are distilled under nitrogen from benzophenone ketyl. Other solvents and chemicals from commercial sources are used without further purification, except as noted.

5-Methoxymethyl-2,2,5-trimethyl-1,3-dioxane (**6**).[9] Fresh cut sodium metal (5.35 g, 232.6 mmol) was added to a solution of ketal alchohol **5** (39.30 g, 245.6 mmol) in toluene (110 mL) under nitrogen. This mixture was heated to reflux for 20 h until all sodium was disappeared. The solution was allowed to cool to room temperature and methyl iodide (15.4 mL, 246.2 mmol) was added. White solid formed immediately and the reaction mixture was heated to reflux for another 3 h. The mixture was filtered and the filtrate was distilled under water aspirator pressure. Fraction with bp 84 – 86°C was collected and identified as the desired product **6** (26.9 g, 63%): ^{1}H NMR δ 3.68 (d, J = 12 Hz, 2 H), 3.51 (d, J = 12 Hz, 2 H), 3.37 (s, 2 H), 3.33 (s, 3 H), 1.40 (s, 3 H), 1.37 (s, 3 H), 0.87 (s, 3 H).

2-Methoxymethyl-2-methylpropan-1,3-diol (**7**).[10] A mixture of **6** (26.9 g, 154.6 mmol), water (12 mL, 666.7 mmol), and 3 drops of concentrated hydrochloric acid in THF (55 mL) was heated to reflux for 30 min. Solvent and water was removed under vacuum and the residue was distilled to give **7** as a clear, colorless liquid (18.5 g, 95%): bp 84–85°C/0.1–0.2 mmHg; IR (neat) 3372 cm^{-1} (br); ^{1}H NMR δ 3.70 (d, J = 11 Hz, 2 H), 3.60 (d, J = 11 Hz), 3.37 (s, 2 H), 3.33 (s, 3 H), 3.07–2.90 (broad, 2 H), 0.83 (s, 3 H).

2,2-Di(chloromethyl)-1-methoxypropane (**8**). To a solution of diol **7** (5.0 g, 37.31 mmol) in dry pyridine (10 mL, 9.78 g, 123.6 mmol) was added distilled thionyl chloride (13.6 mL, 22.18 g, 186.4 mmol) at room temperature with stirring. This solution was heated at 80–90°C for 4 h. The reaction mixture was quenched with water (50 mL) and extracted with ether (50 mL × 3). The ether extracts were washed with saturated sodium bicarbonate solution and brine, dried and concentrated. The residue was distilled under water aspirator pressure to give **8** as clear, colorless liquid (3.66 g, 58%): bp 73–76°C/6–8 cmHg; ^{1}H NMR δ 3.55 (s, 4 H), 3.35 (s, 2 H), 3.28 (s, 3 H), 1.08 (s, 3 H).

Anal. Calcd for $C_6H_{12}OCl_2$: C, 42.13; H, 7.07. Found: C, 41.88; H, 7.46.

2,2-Bis(diphenylphosphinomethyl)-1-methoxypropane (**2**). To a round-bottomed flask was placed triphenylphosphine (7.69 g, 29.3 mmol) in THF (80 mL) under nitrogen atmosphere. Fresh-cut lithium (1.03 g, 147.7 mmol) was washed with hexane and allowed to fall directly into the above solution. This lithium suspension solution was stirred and became deep red color in a few minutes. This mixture was stirred overnight and then filtered to remove excess lithium. The filtration was conducted by passing phosphide anion solution through a pre-dried glass-wool into a second degassed flask. The red solution was cooled to 0°C and *t*-butyl chloride (3.2 mL, 2.72 g, 29.42 mol) was added dropwise to destroy phenyl lithium. Compound **8** (1.24 g, 7.25 mmol) in THF (4 mL) was then added to the phosphide anion solution slowly. The resulting solution was refluxed for 20 h and degassed water (35 mL) was added. The organic portion was separated and the aqueous layer was washed with THF (20 mL × 2). The combined organic portions were dried and concentrated. Excess of diphenylphosphine was distilled off under high vacuum. The residue was chromatographed on silica gel with elution of hexane-dichloromethane to give **2** as viscous oil (2.27 g, 64%): ^{1}H NMR δ 7.80–7.30 (m, 20 H), 3.15 (s, 2 H), 2.88 (s, 3 H), 2.30 (d, J_{P-H} = 3 Hz, 4 H), 1.00 (s, 3 H); ^{13}C NMR (partial) δ 79.44 (t, J = 8.3 Hz), 39.27 (dd, J = 17.4, 9.8 Hz), 38.64 (t, J = 13.6 Hz), 24.96 (t, J = 9.8 Hz); ^{31}P NMR δ–25.12.

Anal. Calcd for $C_{30}H_{32}OP_2$: C, 76.58; H, 6.85. Found: C, 76.54; H, 7.07.

While the elution of hexane-ethyl acetate afforded 4-hydroxybutyldiphenylphosphine **10** (0.56 g) as a clear liquid: ^{1}H NMR δ 7.45–7.00 (m, 10 H), 3.43 (t, J = 6 Hz, 2 H), 2.00–1.85 (br, 3 H), 1.75–1.10 (m, 4 H); ^{31}P NMR δ–16.21.

Anal. Calcd for $C_{16}H_{19}OP$: C, 74.43; H, 7.36. Found: C, 74.06; H, 7.54.

1-Methoxy-2,2-bis(p-toluenesulfonyloxymethyl)propane (**11**). A solution of *p*-toluenesulfonyl chloride (21.10 g, 110.76 mmol) in dry pyridine (35 mL) was added to a solution of **7** (5.10 g, 38.06 mmol) in dry pyridine (15 mL). The mixture was heated on a steam bath for 30 min, then poured into ice water. The suspension was extracted with either (35 mL × 3). The combined extracts were washed with 6 N hydrochloric acid, saturated sodium bicarbonate solution and brine, and dried. Crystallization from methanol gave **11** as a white crystalline solid (14.37 g, 85%): mp 66–68°C; ^{1}H NMR δ 7.55 (d, J = 8 Hz, 2 H), 7.36 (d, J = 8 Hz, 2 H), 3.82 (s, 4 H), 3.12 (s, 2 H), 3.08 (s, 3 H), 2.43 (s, 6 H), 0.90 (s, 3 H); IR ($CDCl_3$) 1359, 1179 cm^{-1}.

Anal. Calcd for $C_{20}H_{26}O_7S_2$: C, 54.30; H, 5.92. Found: C, 54.51; H, 6.08.

2,2-Bis(phenylthiomethyl)-1-methoxypropane (**3**). Sodium (0.68 g, 29.56 mmol) was added to absolute alchohol (50 mL) at ice-water bath temperature. After all sodium reacted, thiophenol (3.40 g, 30.91 mmol) was added to the above solution with stirring for 0.5 h. Tosylate **11** (4.00 g, 9.66 mmol) was then added directly to the solution and the resulting mixture was refluxed for 20 h. After removal of solvent under reduced pressure, the residue was dissolved in 10% sodium hydroxide solution and extracted with ether (60 mL × 3). The extracts were combined, washed with brine, and dried. The crude reaction product was chromatographed on silica gel with eluent of hexane and hexane-dichloromethane. The fraction of hexane-dichloromethane gave **3** as a clear, colorless liquid (4.52 g, 71%): ^{1}H NMR δ 7.42–7.02 (m, 10 H), 3.22 (s, 2 H), 3.10 (s, 3 H), 3.06 (s, 4 H), 1.06 (s, 3 H); ^{13}C NMR δ 137.43, 129.28, 128.69, 125.74, 76.76, 58.66, 41.61, 40.90, 21.27.

Anal. Calcd for $C_{18}H_{22}OS_2$: C, 67.88; H, 6.96. Found: C, 68.06; H, 7.09.

ACKNOWLEDGMENT

Financial support from the National Science Council (NSC77-0208-M002-49) is gratefully acknowledged.

REFERENCES

1. For recent review in tripodal polytertiary phosphines see: L. Sacconi and F. Mani in G. A. Melson and B. N. Figgis Eds., *Transition Metal Chemistry*, Marcel Decker, New York, **8**, 179 (1982).
2. A. A. Ismail and I. S. Butler, *J. Organomet. Chem.* **346**, 185 (1988); J. R. Bleeke, M. K. Hays and R. J. Wittenbrink, *Organometallics* **7**, 1417 (1988); B. S. McGilligan, L. M. Venanzi and M. Wolfer, *Organometallics* **6**, 946 (1987); G. V. Goeden; J. C. Huffman and K. G. Caulton, *Inorg. Chem.* **25**, 2484 (1986); M. D. Vaira, M. Peruzzini and P. Stoppioni, *Polyhedron* **5**, 945 (1986); P. Peringer and M. Lusser, *Inorg. Chim. Acta* **117**, L25 (1986); S. C. Abrahams, A. P. Ginsberg, T. F. Koetzle, P. Marsh and C. R. Sprinkle, *Inorg. Chem.* **25**, 2500 (1986); S. I. Hommeltoft, A. D. Cameron, T. A. Shackleton, M. E. Fraser, S. Fortier and M. C. Baird, *Organometallics* **5**, 1380 (1986); O. J. Scherer, R. Walter and W. S. Sheldrick, *Angew. Chem. Int. Ed. Engl.* **24**, 525 (1985); F. Cecconi, C. A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini and Rimmelin, P. Lemoine, M. Gross, A. A. Bahsoun and J. A. Osborn, *Nouv. J. Chim.* **9**, 181 (1985); D. J. Darensboug and D. J. Zalewski, *Organometallics* **4**, 92 (1985); R. B. King, P. N. Kapoor and R. N. Kapoor, *Inorg. Chem.* **10**, 1841 (1971); J. Chatt, F. A. Hart and H. R. Watson, *J. Chem. Soc.* 490 (1962), and references therein.
3. D. P. Riley and J. D. Oliver, *Inorg. Chem.* **25**, 1814 (1986); K. Brodersen, W. Rolz, G. Jordan, R. Gerbeth and J. Ellermann, *Chem. Ber.* **111**, 132 (1978); C. M. Thorne, S. C. Rawle, G. A. Admans and S. R. Cooper, *J. Chem. Soc., Chem. Commun.* 306 (1987).
4. P. Janser, L. M. Venanzi and F. Bachechi, *J. Organomet. Chem.* **296**, 229 (1985), and references therein.
5. C. Bianchini, A. Meli, F. Laschi, A. Vacca and P. Zanello, *J. Am. Chem. Soc.* **110**, 3919 (1988).
6. A. J. McAlees, R. McCrindle and A. R. Woon-Fat, *Inorg. Chem.* **15**, 1065 (1976).
7. A tripodal terdentate with phosphorus and sulfur donor atoms, 2,2-bis(phenylthiomethyl)-1-diphenylphosphinopropane has been synthesized in this group. Manuscript in preparation.
8. V. W. Gash, *J. Org. Chem.* **37**, 2197 (1972).
9. L. K. Yuldasheva, A. V. Bogatskii, R. P. Arshinova and L. I. Spirina, *Zh. Org. Khim.* **1968**, 4, 1874.
10. A. V. Bogatskii, A. I. Gren, S. P. Egorrova, G. I. Goryashina, Z. D. Bogatskaya and N. L. Garkovik, *Mater, Vses. Din. Stereokhim. Konformationnomu Anal.*, 1st **1970**, 65–9; *Chemical Abstract* **1974**, 80, 81626k.