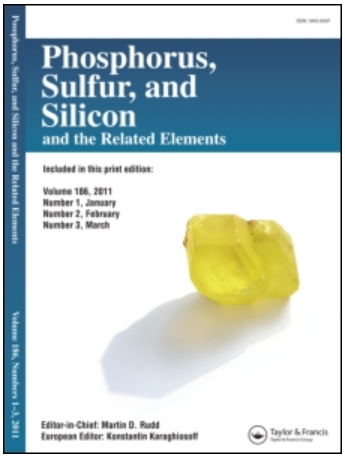

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SYNTHESIS AND CRYSTAL STRUCTURE OF *TRANS*-1,4-BIS(DIPHENYLPHOSPHINO)-1,3-BUTADIENE

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SYNTHESIS AND CRYSTAL STRUCTURE OF *TRANS*-1,4-BIS(DIPHENYLPHOSPHINO)-1,3-BUTADIENE

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The synthesis of *trans*-1,4-bis(diphenylphosphino)-1,3-butadiene (**1**) was accomplished via the reaction of lithium diphenylphosphide with 1,1,2,3,4,4-hexachlorobutane. Crystals suitable for X-ray diffraction were acquired by slow evaporation of solvent. Compound **1** crystallized in the monoclinic space group $P2_1/n$ (14), a = 9.068(2) Å, b = 25.862(5) Å, c = 10.068(5) Å, β = 107.69(3)°, V = 2249(2) Å^3, Z = 4. Compound **1** shows the diphenylphosphino units attached to the 1 and 4 carbons of a 1,3-butadiene spacer separated by 7.2 Å. Compound **1** reacts with two equivalents of the $W(CO)_5$(THF) to yield ditungstendecacarbonyl-[μ-1,4-bis(diphenylphosphino)-1,3-butadiene] (**2**).

Keywords: Bis(diphenylphosphino)butadiene; diphosphine ligand; tungsten phosphine complex; x-ray structure

INTRODUCTION

The use of bidentate phosphines as ligands in organometallic chemistry is pervasive,[1–6] and has been recently reviewed.[7–10] A vast number of organophosphines are currently available commercially, and well established methods for their synthesis are reported.[2,11–17] Phosphine ligands play a major role in modern coordination chemistry, as they are particularly well suited to binding transition metals, in low oxidation states.[18] The synthesis of new phosphine ligands and the catalytic properties of organometallic compounds prepared from these ligands are areas of ongoing interest in our laboratory.[19–22] The synthesis of

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phosphines by direct coupling reactions between haloorganic compounds and alkali metal phosphides or Grignard reagents is a prevalent method of phosphine synthesis.[23–25] Direct coupling is still widely utilized as a route to higher derivatized polydentate phosphines. We report the direct coupling of lithium diphenylphosphide with 1,1,2,3,4,4-hexachlorobutane to afford *trans*-1,4-bis(diphenylphosphino)-1,3-butadiene, (**1**). Compound **1** was structurally characterized by X-ray crystallography and its ligating properties were studied.

EXPERIMENTAL

General Procedures

All reactions and manipulations were carried out under nitrogen using standard Schlenk and dry box techniques. Solvents were degassed and purified by distillation under nitrogen from the appropriate drying agents (sodium/benzophenone for THF, sodium for toluene, CaH_2 for CH_2Cl_2 and hexanes). Organic solvents were dried and degassed using standard procedures. The starting materials 1,1,2,3,4,4-hexachlorobutane, n-butyllithium, and diphenylphosphine were purchased from the Aldrich Chemical Company and used without further purification. $W(CO)_6$ was purchased from Aldrich Chemical Company and sublimed prior to use. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer and referenced to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra were recorded on QE-300 and Varian XL-200 spectrometers at 121.4 MHz and 80.98 MHz, respectively, with chemical shifts reported in ppm referenced to external H_3PO_4. ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer at 50.2 MHz. Infrared spectra were recorded on Perkin Elmer 1710 or Mattson Research Series Infrared Fourier Transform Spectrometers. Mass spectroscopy was obtained using chemical ionization.

Preparation of 1,4-bis(diphenylphosphino)-1,3-butadiene (1)

Lithium diphenylphosphide (1.08 g, 5.6 mmol) was dissolved in THF (100 mL) and added slowly over 2 h to a solution of 1,1,2,3,4,4-hexachlorobutane (0.373g, 1.41 mmol) in THF (100 mL) at −78°C. After addition, the reaction was warmed to room temperature and the solvent volume reduced to 50 mL under vacuum. Deionized water (50 mL) was added, the layers allowed to separate, and the organic layer removed. Removal of solvent affords an oil. The oil was dissolved in toluene and addition of hexane gave a white solid (**1**). Yield 0.127

g (28%). ^{1}H NMR (CD_2Cl_2, δ, ppm) 6.5 [m, 4H, (-C*H*=C*H*-C*H*=C*H*-), 7.5 [m, 20H, C_6H_5]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ, ppm) −10.2 (s); MS(CI) (m/z): 423 (MH^+), 439 (MH^+O), 455 (MH^+O_2). ^{13}C NMR (CD_2Cl_2, δ, ppm) 143.8 [dd, -*C*H=CH-, $^1J_{PC}$ = 23.4 Hz, $^4J_{PC}$ = 10.6 Hz], 136.1 Hz [dd, =*C*H-*C*H=, $^2J_{PC}$ = 20.6 Hz, $^3J_{PC}$ = 8.1 Hz,], Phenyl: 138.6 Hz [d, *C (1)*, $^1J_{PC}$ = 10.6 Hz], 134.0 Hz [d, *C (2)*, $^2J_{PC}$ = 20.6 Hz], 129.5 Hz [d, *C (3)*, $^3J_{PC}$ = 7.5 Hz], 129.7 Hz [s, *C(4)*, $^4J_{PC}$ < 1 Hz].

Preparation of ditungstendecacarbonyl-[μ-1,4-bis(diphenylphosphino) -1,3-butadiene], 2

Tungsten pentacarbonyl tetrahydrofuran solvento species, $W(CO)_5THF$, was synthesized by photolysis of freshly sublimed tungsten hexacarbonyl (0.7 g, 2.0 mmol) in 100 mL of THF. An excess of $W(CO)_5THF$ was then added to a solution of compound **1** (0.1 g, 0.237 mmol) in THF. The solution was allowed to stir overnight. Compound **2**, a yellow solid, was isolated by taking the solution to dryness. Yield 0.17 g (50%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ, ppm) 10.5 ppm (s) ($^1J_{P\text{-}W}$ = 238.7 Hz); IR(KBr): $\nu_{(CO)}$ = 2072(m), 1989(sh), 1925(s) cm^{-1}.

X-ray Structure Data of 1

A crystal of **1** was grown by slow evaporation of methylene chloride. Data were collected using a Enraf-Nonius CAD4 computer axis diffractometer. The structure was partially solved by using the structure solution program SHELX-86 and the remaining atoms were located in succeeding difference Fourier syntheses. Refinement was done using MolEN. Hydrogen atom positions were added to the structure factor calculations but their positions were not refined. The crystallographic data are summarized in Table I. Selected bond lengths and angles are listed in Table II.

RESULTS AND DISCUSSION

Compound **1** was obtained from the reaction of six equivalents of lithium diphenylphosphide with 1,1,2,3,4,4-hexachlorobutane. In addition to **1**, the reaction produces two equivalents of (tetraphenyl)biphosphine. The formation of (tetraphenyl)biphosphine can be accounted for by the elimination of PPh_2Cl during the course of the reaction and its combination with $LiPPh_2$.[26] A similar mechanism has been reported for the reaction of lithium diphenylphosphide with bro-

TABLE I Summary of crystallographic data for **1**

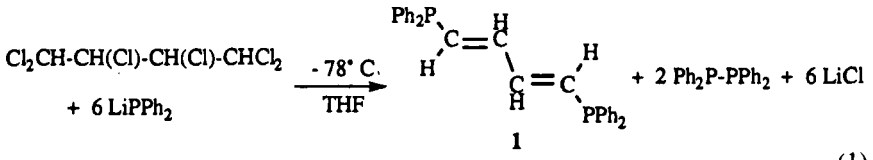
formula	$P_2C_{28}H_{24}$
fw	422.45
cryst size, mm	0.5 × 0.24 × 0.19
cryst system	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	9.068(2)
b, Å	25.862(5)
c, Å	10.068(5)
β, deg	107.69(3)°
V, Å^3	2249(2)
Z	4
temp, °C	−67.0
D_{calc}, g cm^{-3}	1.247
μ, cm^{-1}	2.00
radiation (λ, Å)	Mo K_α (0.71073)
reflcns measd	3016 ($\pm h$, k, l)
relcns used	1881 with $I > 3\sigma(I)$
variables	271
R	0.079
R_w	0.092

$R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$

minated alkenes.[27] Extraction of the organic layer and recrystallization from toluene/hexane affords **1** as a white crystalline solid in 25–30% yield. The overall synthesis of **1** is summarized in Eq. 1.

TABLE II Selected bond distances (Å) and bond angles (deg) for **1**

P(1)-C(1)	1.805(7)	P(2)-C(221)	1.845(7)
P(1)-C(111)	1.834(6)	C(1)-C(2)	1.331(9)
P(1)-C(121)	1.839(7)	C(2)-C(2)	1.45(1)
P(2)-C(3)	1.810(8)	C(3)-C(4)	1.343(9)
P(2)-C(211)	1.825(7)	C(4)-C(4)	1.46(1)
C(1)-P(1)-C(111)	100.7(3)		
C(1)-P(1)-C(121)	104.2(3)		
C(111)-P(1)-C(121)	101.6(3)		
C(3)-P(2)-C(211)	101.0(3)		
C(3)-P(2)-C(221)	103.5(3)		
C(211)-P(2)-C(221)	101.0(3)		
P(1)-C(1)-C(2)	120.7(6)		
C(1)-C(2)-C(2)	124.6(9)		
P(2)-C(3)-C(4)	119.1(6)		
C(3)-C(4)-C(4)	122.9(9)		



(1)

Compound **1** has only been cited in the patent literature,[28] although the isomer 2,3-bis(diphenylphosphino)-1,3-butadiene is known.[29] Compound **1** shows a singlet in the $^{31}P\{^1H\}$ NMR spectrum ($\delta = -10$ ppm). The ^1H NMR spectrum shows a complex multiplet centered at 6.5 ppm corresponding to the AA'BB'XX' spin system of the four diene protons coupled to two phosphorus nuclei. This is rather similar to the chemical shift reported for 1,2-bis(diphenylphosphino)ethylene ($\delta = 6.7$ ppm).[30] Compound **1** was also characterized by chemical ionization mass spectroscopy with a parent peak for **1** observed at $MH^+/z = 423$.

An X-ray structure study was carried out on a single crystal of **1**. An ORTEP diagram for **1** is shown in Figure 1. Selected bond distances and bond angles for **1** are listed in Table II. The butadiene unit in **1** is in an (E,E) configuration with the phosphorus atoms *trans* to one another and separated by 7.2 Å. The bond distances between the phosphorus atoms and phenyl carbons are within the range of 1.825(7) to 1.845(7) Å, while the distance between the phosphorus and carbon atoms of the butadiene unit are slightly shorter (1.805(7) and 1.810(8) Å for P1-C1 and P2-C3, respectively). The carbons in the butadiene spacer show sp^2 character with bond angles of ∠P1-C1-C2 = 120.7(6)°, ∠C1-C2-C2′ = 124.6(9)°, ∠P2-C3-C4 = 119.1(6)°, and ∠C3-C4-C4′ = 122.9(9)°. The bond distances between C3-C4 and C1-C2 are 1.343(9) and 1.331(9) Å, respectively. These distances correspond to those observed for C-C double bonds in analo-

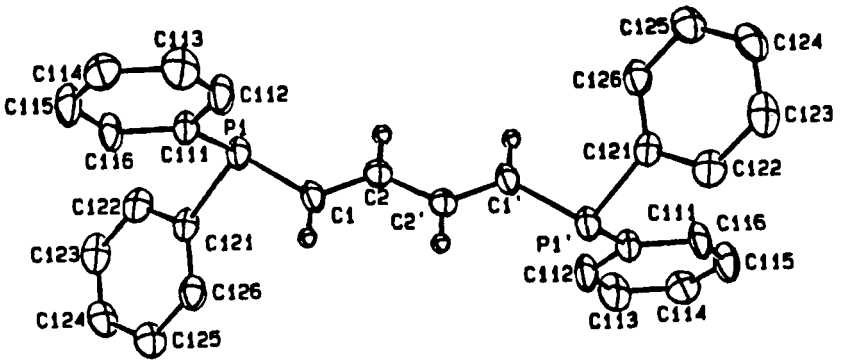
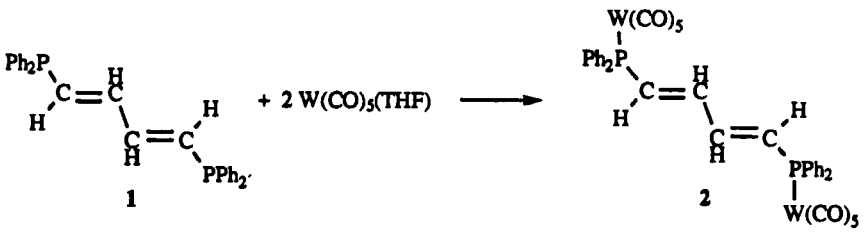


FIGURE 1 Molecular structure of **1** (ORTEP, 50% probability ellipsiods).

gous compounds.[29,31,32] Specifically, the double bond distances in compound **1** are comparable to those seen in a nonsubstituted 1,3-butadiene (1.33(2) Å).[33] The bond distances between C2-C2′(1.45(1) Å) and C4-C4′(1.46((1) Å) are longer and correspond to C-C single bonds.[31,32] The single bond distance in 1,3-butadiene is 1.46(2) Å.[33]

The synthesis and characterization of a number of d^6 bimetallic compounds bridged by diphosphines, $(CO)_5M(\mu\text{-}PPh_2(CH_2)_nPPh_2)M(CO)_5$ (M = Cr, Mo, W; n = 1, 2, 3), have been reported.[34,35] To investigate the ligating abilities of **1**, the reaction of **1** with $W(CO)_5(THF)$ was effected (Eq. 2).



(2)

Ditungstendecacarbonyl-[μ-1,4-bis(diphenylphosphino)-1,3-butadiene] (**2**) shows a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ = 10.5 ppm, with tungsten satellites ($^1J_{P\text{-}W}$ = 238.7 Hz). The ^{31}P NMR chemical shift for **2** moves 20 ppm downfield from free **1**, and is consistent with previously reported values for analogous complexes.[35–37] The IR spectrum shows characteristic υ_{CO} absorption bands (υ_{CO} = 2072 (m), 1989 (sh), and 1925 (s) cm^{-1}) that coincide with other tungstenpentacarbonyl phosphine complexes.[36,37] The frequency of the υ_{CO} bands indicates that **1** has similar electronic properties to dppm, dppe, and PPh_2Me (υ_{CO} = 2072 ± 2 (m), 1983 ± 3 (w), and 1940 (s) cm^{-1}).[37]

CONCLUSION

The synthesis of 1,4-bis(diphenylphosphino)-1,3-butadiene **1** was accomplished using a direct coupling method. The X-ray crystal structure of **1** was obtained and shows an (E, E) configuration for the butadiene unit, with the phosphorus atoms in a *trans* configuration and separated by 7.2 Å. A preliminary study of the reactivity of **1** with $W(CO)_5(THF)$ was carried out, and further work is in progress.

Acknowledgment

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Supporting Material Available

Tables of positional parameters, general temperature factor expressions, bond distances and angles, listings of observed and calculated structure factors for **1** are available. Ordering information is given on any current masthead page.

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