3608 *Organometallics* **2008,** *27,* 3608–3610

Notes

Synthesis of a Novel Bisphosphonium Salt Based on 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl (Binap)

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Received February 28, 2008

Summary: The reaction between 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (Binap) and an equimolar amount of [Cu(OTf)$_2$] (where OTf = trifluoromethylsulfonate) in acetonitrile afforded the new bisphosphonium salt **1** *by a mechanism that must involve two C−H bond activations and the consequent intramolecular formation of two new C−P bonds. Compound* **1** *was characterized by spectroscopic and X-ray diffraction methods.*

Organic cations, such as quaternary ammonium and phosphonium salts, are used in many fields of chemistry, due to their use as functional materials.[1] In addition, the unique feature of quaternary phosphonium salts as ionic liquids remains an active research area. Accordingly, new reactions are continuously being developed for the preparation of phosphonium compounds.[2] In contrast to quaternary ammonium salts, the functional properties of phosphonium salts have been less investigated. This fact is attributed, in part, to the more difficult synthesis of phosphonium salts compared with the corresponding nitrogen compounds.[3] Here we report the one-step synthesis and characterization of a novel bisphosphonium salt.

The coordination chemistry of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (Binap) with different metal complexes has been extensively studied[4] and also there are many examples of oxidation of the P atoms.[5]

Despite extensive research focused on Binap metal complexes, processes that involve C−P intramolecular bond formation have not been reported. We unexpectedly succeeded in isolating a new kind of phosphonium salt (compound **1**; see Scheme 1) generated by double C−P intramolecular bond formation and C−H activation.

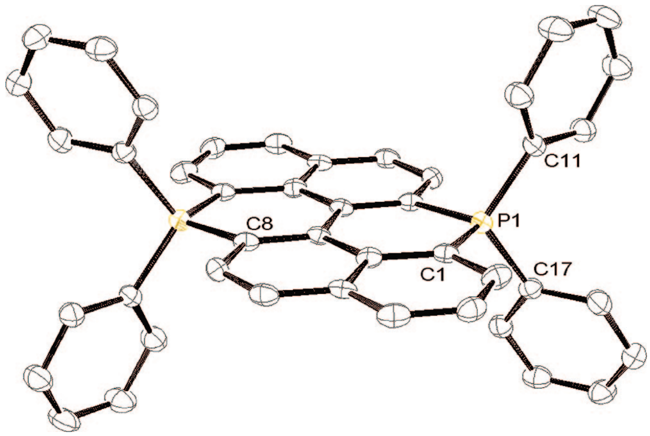

Figure 1. Structure of the cation in the molecule **1**. Displacement ellipsoids are scaled to the 50% probability level. The hydrogen atoms and the OTf$^-$ ions are not shown.

The addition of Binap to [Cu(OTf)$_2$] in acetonitrile, under aerobic conditions, caused a change in the color of the solution (from blue to yellow). The reaction was monitored by ^{31}P NMR, and the spectrum in CD$_3$CN of the crude reaction mixture showed the presence of three different compounds. One was identified as the monoxide of Binap (Binapo),[6] while a broad second signal at 2.1 ppm was assigned to the complex [Cu(Binap)(NCMe)$_2$](OTf) (**2**), where a reduction of Cu(II) to Cu(I) had occurred (similar complexes were previously reported).[7] A singlet at 4.0 ppm, which has the same ratio as that for Binapo, corresponded to the phosphonium salt **1**. Compound **1**, which is air and moisture stable, was purified by silica chromatography using dichloromethane/methanol (9:1). After removal of the solvent, it was isolated as a yellow solid in 24% yield. Compound **1** was characterized in solution by means of NMR (^{1}H, ^{13}C, and ^{31}P) and mass spectroscopy. The structure of the product could not be completely inferred from the spectroscopic data alone, and thus a single crystal of **1** was subjected to X-ray diffraction analysis, with the results summarized in Figure 1 and Table 1.

The analysis of this structure shows that two C−P bonds have been formed, along with two new rings consisting of one P atom

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10.1021/om800191b CCC: $40.75

Scheme 1. Synthesis of Compound 1

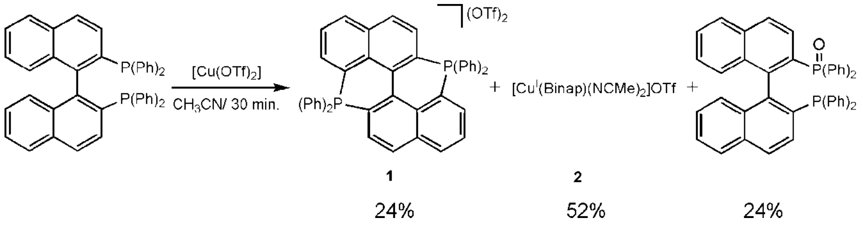


Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

Bond Lengths			
P(1)−C(1)	1.770(3)	P(1)−C(17)	1.787(3)
P(1)−C(8′)	1.773(3)	P(1)−C(11)	1.792(3)
Bond Angles			
C(1)−P(1)−C(8′)	106.37(14)	C(1)−P(1)−C(11)	111.72(14)
C(1)−P(1)−C(17)	110.60(14)	C(8′)−P(1)−C(11)	108.19(13)
C(1′)−P(1)−C(17)	109.33(14)	C(17)−P(1)−C(11)	110.50(14)

and five C atoms. The binaphthalene aromatic system is planar, while the phenyl groups are orthogonal to that plane. Both phosphorus atoms display a slightly distorted tetrahedral coordination environment (e.g., C(1)−P(1)−C(17) = 110.60(14)° or C(8′)−P(1)−C(11) = 108.19(13)°). In each P atom both P−C(naphthalene) lengths are similar (P(1)−C(1) = 1.770(3) Å and P(1)−C(8′) = 1.773(3) Å) and are slightly shorter than the corresponding P−C(phenyl) lengths (P(1)−C(11) = 1.792(3) Å and P(1)−C(17) = 1.787(3) Å). The C═C lengths inside the naphthalene ring are in agreement with the retention of the aromatic structure.

Therefore, in compound **1** the intramolecular formation of two new C−P bonds has occurred on the basis of two formal C−H activations. The reaction was also set up under inert conditions, and the ^{31}P NMR spectrum did not show the presence of the compound **1**; therefore, we propose the mechanism in Scheme 2. The reaction starts with the reduction of Cu(II) to Cu(I), after which the presence of oxygen causes the abstraction of one hydrogen atom. The repetition of that process leads to the formation of **1** and the subsequent elimination of H_2O_2. However, we wish to stress that in the absence of mechanistic studies, which have not been carried out, no final conclusions regarding the mechanism can be made.

In summary, we have successfully developed an unprecedented bisphosphonium salt where the activation of two aromatic C−H bonds causes the intramolecular formation of two C−P bonds. The compound is air and moisture stable. The scope of this class of phosphorus compounds and their applications as ionic liquids are currently under investigation in our laboratory.

Experimental Section

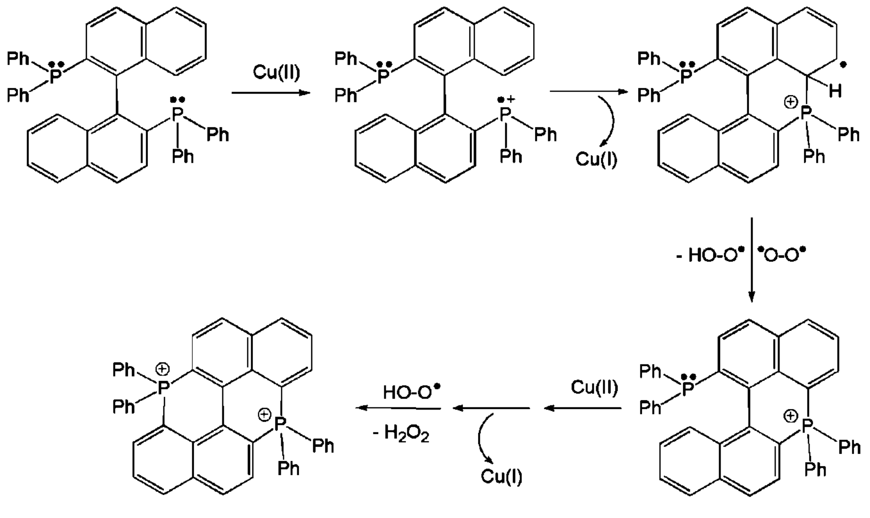
General Procedures. ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer and ^{1}H NMR and ^{31}P NMR on a Varian Unity Plus 300 spectrometer. High-resolution mass spectra were obtained at the University of Texas at Austin, Department of Chemistry and Biochemistry, Mass Spectrometry Facility. Reagents were used as purchased from various commercial sources.

Synthesis of Compounds 1 and 2. A mixture of $[Cu(OTf)_2]$ (0.058 g, 0.16 mmol) and Binap (0.100 g, 0.16 mmol) in acetonitrile (20 mL) was stirred at room temperature for 30 min.

Compound 1. The reaction mixture was purified by silica gel chromatography employing dichloromethane/methanol (9:1). The eluting yellow band was collected, and the resulting solution was concentrated under vacuum to a volume of 5 mL. Addition of diethyl ether (20 mL) caused the precipitation of compound **1** as a microcrystalline solid, which was washed with hexane (2 × 20 mL). Slow diffusion of diethyl ether into a concentrated solution of **1** in acetonitrile afforded crystals, one of which has been used for the structural determination by means of X-ray diffraction. Yield: 0.030 g, 24%. ^{1}H NMR (acetone-d_6, 300 MHz): δ 8.96−8.93 (m, 4H), 8.39−8.32 (m, 4H), 8.03−7.79 (m, 22H). ^{13}C{^{1}H} NMR (acetone-d_6, 400 MHz): δ 140.0 (m), 139.2 (s), 136.2 (s), 135.2 (s), 135.0 (s), 134.9 (s), 131.0 (s), 130.9 (s), 130.5 (s), 130.4 (m), 122.7 (s), 119.7 (s), 119.5 (s), 118.8 (s). ^{31}P NMR (acetone-d_6, 300 MHz): δ 4.0 (s). HR ESI-MS: (M + 1) m/z 310.0912 ± 0.002 (calcd for $C_{44}H_{30}P_2^{2+}$ 310.0906).

Compound 2. Purification by silica gel chromatography of the same crude reaction mixture using dichloromethane permits the isolation of compound **2**. A second yellow band was eluted,

Scheme 2. Mechanism Proposed for the Formation of 1



and this fraction was collected and concentrated under vacuum to a volume of 5 mL; addition of diethyl ether (20 mL) caused the precipitation of the compound **2** as a microcrystalline solid. It was washed with hexane (2 × 20 mL). Yield: 0.076 g, 52%. ^{1}H NMR (400 MHz, CD_3CN): δ 7.88 (m, 4H), 7.68−7.61 (m, 10H), 7.38−7.27 (m, 4H), 7.23−7.17 (m, 4H), 7.11−7.06 (m, 2H), 6.80−6.71 (m, 4H), 6.67−6.62 (m, 4H). ^{13}C NMR (400 MHz, CD_3CN (J, Hz)): δ 139.0 (m), 135.0 (t (9.2)), 133.5 (t (3.8)), 133.3 (m), 132.6 (t (17.3)), 132.1(t (13.4)), 131.0 (s), 129.4 (m), 128.8 (m), 128.0 (s), 127.7 (t (5.4)), 127.4 (s), 127.1 (m), 126.6 (d (35.4)). ^{31}P NMR (300 MHz, CD_3CN): δ 2.1 (broad). HR ESI-MS: (M + 1) m/z 685.1275 ± 0.002 (calcd for $C_{44}H_{32}CuP_2$ 685.1270).

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. GM77437). S.N. thanks the Spanish Ministry of Education and Science for a postdoctoral fellowship.

Supporting Information Available: A CIF file giving X-ray crystallographic data for compound **1** and text and a table giving details of the X-ray structural study. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800191B