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Preparation and Characterization of $\{3\text{-}[2\text{-}Pd(\mu\text{-}Cl)\text{-}4\text{-}MeO\text{-}C_6H_3\text{-}]syd\text{-}P(Bu^t)_2\}_2$

Shaw-Tao Lin,*[†] Hung-Sheng Cheo,[†] Lin-Shuh Liu,[‡] and Ju-Chun Wang*[‡]

Department of Applied Chemistry, Providence University, Sha-Lu, Taichung Hsien,
Taiwan 433-01, ROC, and Department of Chemistry, Soochow University,
Taipei 111-01, ROC

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*Summary: A dimer of a six-membered metallacycle [Pd-(C-P)X]$_2$ (**2**) was prepared by reacting PdCl$_2$ with 3-(4-methoxyphenyl)-4-(di-tert-butylphosphino)sydnone in an ethanol solution at 80 °C. This is the first report of the activation of a C−H bond in the arylsydnone system. The molecular structure of compound **2** was determined by a single-crystal X-ray crystallographic study.*

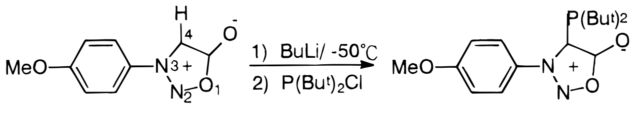
Introduction

Ever since the first cyclometallation reactions were described,[1] there has been interest in this process because it permits the selective activation of C−H bonds in heterosubstituted organic molecules.[2] Although a mesoionic sydnone ring bearing an aryl ring resembles heterosubstituted aromatic molecules, there have only been reports of the metalation of a sydnone ring at C(4) with σ bonding. Position C(4) can be functionalized by various functional groups, such as phosphino, silyl, alkyl, halide, etc.[3] On the other hand, various calculations have demonstrated that the oxygen atom of C(5)═O bears a partial negative charge.[4] Due to the combination of the lone-pair electron from the heteroatom at C(4) and the partial negative charge of the oxygen, a sydnone ring can act as a chelate ligand to form a series of five-membered metallocyclic complexes. The reaction of 3-(4-methoxyphenyl)-4-(di-*tert*-butylphosphino)sydnone (**1**) and PdCl$_2$ in an ethanol solution gave a yellow compound. Spectroscopic analysis and single-crystal X-ray structural analysis reveal that this complex was formed from palladium insertion into the C−H bond of the aryl ring. We describe here this insertion into the C−H bond of the arylsydnone. A structural analysis of compound **2** is interesting and merits reporting.

Results and Discussion

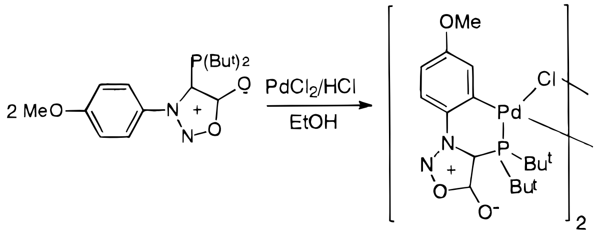
Compound **1** was prepared from the lithiated 3-(4-methoxyphenyl)sydnone, followed by the exchange with di-*tert*-butylchlorophosphine at −50 °C in good yield (Scheme 1).[5]

Scheme 1



1

Scheme 2



2

The air-stable compound **2** was prepared by reacting compound **1** and 1 equiv of PdCl$_2$ in ethanol in the presence of HCl under reflux conditions (Scheme 2). The product precipitated out as the reaction proceeded and was collected by filtration. The IR spectrum of compound **2** shows CO stretches at 1720 cm^{-1}, which is 20 cm^{-1} lower than that in compound **1**, suggesting it has a shorter of C═O bond. The ^{1}H NMR spectrum shows two doublets (δ 7.40 and 7.47 ppm) and one doublet of a doublet (δ 6.70 ppm) for the aromatic hydrogens. This characteristic pattern for the aromatic protons indicates that this is a trisubstituted system. One of the protons showed an upfield shift from δ 7.43 to 6.70 ppm, which further suggests that the third substituent is a metal. This compound did not survive under electron impact mass spectrometry. Using fast atom bombardment mass spectrometry with 3-nitrobenzyl alcohol as the solvent, the highest ions were detected at *m*/*z* 954, the mass of a fragment (corresponding to a protonated dimeric species) of compound **2**. A fragment with mass of 477 is a base peak (double-charged, protonated compound **2**).

A single-crystal structural determination was carried out for compound **2**, which confirmed the formulation suggested by the spectroscopic data above. The palladium complex center is a planar structure and that

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[†] Providence University.

[‡] Soochow University.

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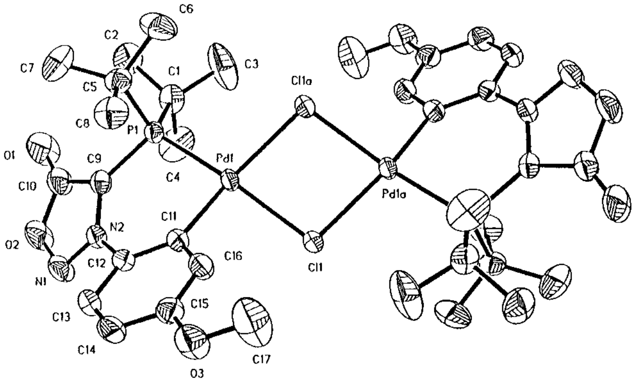

Figure 1. Structure diagram of a single molecule of **2** with the atoms numbered as in Table 1. Hydrogen atoms are omitted for clearity.

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

Pd(1)−Cl(1)	2.437(1)	Pd(1)−P(1)	2.257(1)
Pd(1)−C(11)	1.993(3)	Pd(1)−Cl(1A)	2.443(1)
Cl(1)−Pd(1A)	2.442(1)	P(1)−C(1)	1.903(3)
P(1)−C(5)	1.874(3)	P(1)−C(9)	1.794(3)
O(1)−C(10)	1.207(5)	O(2)−N(1)	1.363(4)
O(2)−C(10)	1.409(5)	N(1)−N(2)	1.306(4)
N(2)−C(9)	1.379(4)	N(2)−C(12)	1.427(3)
C(9)−C(10)	1.430(4)	C(11)−C(12)	1.385(4)
C(11)−C(16)	1.406(4)	C(12)−C(13)	1.400(4)
C(13)−C(14)	1.353(4)	C(14)−C(15)	1.393(5)
C(15)−C(16)	1.372(5)		
Cl(1)−Pd(1)−P(1)	164.4(1)	Cl(1)−Pd(1)−C(11)	92.8(1)
P(1)−Pd(1)−C(11)	89.5(1)	P(1)−Pd(1)−Cl(1A)	102.8(1)
Pd(1)−Cl(1)−Pd(1A)	99.3(1)	Pd(1)−P(1)−C(1)	110.5(1)
Pd(1)−P(1)−C(5)	114.7(1)	C(1)−P(1)−C(5)	113.1(1)
Pd(1)−C(11)−C(12)	132.7(2)	Pd(1)−C(11)−C(16)	111.7(2)

consists of two palladium atoms in the presence of two bridged chlorine ligands, Figure 1. In addition, each palladium atom is coordinated to phosphine and binds with one carbon of the benzene ring. Some of selected bond lengths and bond angles are listed in Table 1.

The bond distances in the sydnone ring show that the N(2)−C(12) and N(1)−O(2) bonds are shorter than those revealed by data obtained in uncoordinated sydnones,[8−10] the N(2)−C(9) and C(9)−C(10) bonds are substantially longer. The angle between the aryl and sydnone ring is much smaller. These findings suggest that the sydnone ring is distorted due to complexing with the palladium metal. The C−C bond lengths in the benzene ring range from 1.353 to 1.430 Å, which reflects severe distortion of the benzene ring due to the influence of bonding with palladium.

Experimental Section

All melting points were measured with a Yanaco MP-J3 apparatus and are uncorrected. ^{1}H NMR and ^{31}P NMR spectra were recorded on a Bruker AC-250 spectrometer at 250 and 101.20 MHz, respectively. IR data were obtained using a Perkin-Elmer 883 spectrophotometer. FAB mass spectra were measured on a JEOL JM5-SX/SX 102A spectrometer, using 3-nitrobenzyl alcohol as a solvent. Microanalyses were performed on a Heraeus CHN-O rapid analyzer. 3-(4-Methoxyphenyl)sydnone was prepared as described in the literature.[11]

Table 2. Crystal Data for $C_{34}H_{48}N_4O_6P_2Cl_2Pd_2$

formula	$C_{34}H_{48}N_4O_6P_2Cl_2Pd_2$
cryst size	0.2 × 0.4 × 0.6
cryst syst	monoclinic
space group	*C*2/*c*
fw	954.4
a, Å	28.857(2)
b, Å	8.8327(4)
c, Å	16.185(1)
β, deg	109.043
V, Å^3	3899.4(4)
Z	4
d_{calcd}, g/cm^3	1.626
μ, mm^{-1}	1.189
no. of reflns measured	3510
no. of unique reflns	3438
no. of obs reflns	3008
criterion for observation	$F > 4\sigma(F)$
R_{int}	0.0194
no. of variables	226
R; R_w^{a}	0.0308; 0.0401
g	0.0005
GOF	1.15
max. shift/σ	0.000
residual electron density, e/Å^3	0.61

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F|)$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$. $w = [\sigma^2(F_o) + gF_o{}^2]^{-1}$.

Preparation of 3-(4-Methoxylphenyl)-4-(diphenylphosphino)sydnone. Under an argon atmosphere, *n*-BuLi in hexane (3.0 mL, 1.6 M, 0.48 mmol) was added to 3-(4-methoxyphenyl)sydnone (81 mg, 0.42 mmol) in a THF (15 mL) solution at −50 °C. After the mixture was stirred at that temperature for 30 min, di-*tert*-butylchlorophosphine (0.8 mL, 0.42 mmol) was added dropwise. After the mixture was stirred at that temperature an additional 4 h, the mixture was warmed to room temperature for another 2 h to ensure a complete reaction. A solid was obtained after the mixture was poured into water and filtered. The light yellow crystals from a CH_2Cl_2 solution gave 119 mg (84.3%) of compound **1**. Mp 105−106 °C. IR (KBr): 1739 cm^{-1} (ν_{CO}). ^{1}H NMR (CDCl$_3$): δ 1.27 (s, 9H), 1.37 (s, 9H), 3.69 (s, 3H, OMe), 7.01 (d, J = 9.0 Hz, 2H), 7.46 (d, J = 9.0 Hz, 2H). ^{31}P NMR (CDCl$_3$): δ 4.44. EI-MS: *m*/*z* 336 (M$^+$, 48), 280 (M$^+$ − NO − CO, 36), 57 ($C(CH_3)_3{}^+$, 100). Anal. Calcd for $C_{17}H_{25}N_2O_3P$: C, 60.70; H, 7.49; N, 8.33. Found: C, 60.91; H, 7.15; N, 8.49.

Preparation of Compound 2. A mixture of $PdCl_2$ (35.4 mg, 0.2 mmol) in HCl (concentrated, 8 mL) and compound **1** (67.2 mg, 0.2 mmol) in EtOH (8.0 mL) was heated at 80 °C for 4 h. The yellow solid was filtered off and then recrystallized from CH_2Cl_2, by the aid of diffusion with diethyl ether, to give 70.6 mg (74% yield) of compound **2** as yellow crystals. Mp 188−189 °C. IR (KBr): 1720 cm^{-1} ν_{CO}. ^{1}H NMR (CDCl$_3$): δ 1.40 (s, 9H), 1.47 (s, 9H), 3.82 (s, 3H), 6.70 (dd, J = 8.7, 2.5 Hz); 7.40 (d, J = 8.7 Hz), 7.47 (d, J = 2.5 Hz). ^{31}P NMR (CDCl$_3$): δ 58.12 (s). FAB-MS: *m*/*z* 954 ((M + 1)$^+$, 10), 919 ((M + 1 − Cl)$^+$, 43), 477 ((M + 1)$^{2+}$, 100). Anal. Calcd for $C_{34}H_{48}Cl_2N_4O_6P_2Pd_2Cl_2$: C, 42.79; H, 5.08; N, 5.89. Found: C, 42.57; H, 5.10; N, 6.11.

Crystal Data for $C_{34}H_{48}Cl_2N_4O_6P_2Pd_2$. M_w = 954.4 Å. Monoclinic, space group *C*2/*c*. a = 28.857(2) Å, b = 8.8327(4) Å, c = 16.185(1) Å, α = 90.0 °, β = 109.043(4)°, γ = 90.0°, V = 3899.4(4) Å^3, Z = 4, d_{calcd} = 1.626 g/cm^{-3}, μ(Mo Kα) = 1.189 mm^{-1}, = 0.710 73 Å. A yellow crystal of approximately 0.2 × 0.4 × 0.6 mm was mounted on a glass fiber for X-ray structural analysis. Cell constants were derived from a least-squares refinement of 25 high-angle reflections with 11° < 2θ < 26°. Intensity data were collected using a ω scan mode on a Siemens P4 diffractometer equipped with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). A total of 3438 unique reflections were measured, of which 3008 were observed ($F > 4\sigma(F)$). An empirical absorption correction based on a series of ψ-scans was applied to the data. Three standard reflections were measured every 300 reflections, and only small

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(<4%) random variations were observed. Lorentz and polarization corrections were applied.

The structure was determined by the heavy-atom method using the SHELXTL-PLUS software package.[6] The palladium atom position was revealed on a Patterson map. All other atoms were located from subsequent Fourier difference syntheses. H-atoms were treated as the normal atoms and were refined isotropically. The structure was refined by the full-matrix least-squares method. Heavy atoms were refined anisotropically. $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma^2(F_o) + 0.0025F_o^2]$. Refinement converged to $R = 0.0306$, $R_w = 0.0422$, and $S = 0.74$, based on 322 variables and 3008 reflections. Details of the crystal data are listed in Table 2.

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Supporting Information Available: Complete tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and H-atom coordinates (5 pages). Ordering information is given on any current masthead page.

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