

Preliminary communication

SULFUR YLIDE COMPLEXES OF PALLADIUM, PREPARATION OF ORGANOMETALLIC COMPOUNDS BY THE PHASE TRANSFER CATALYSIS TECHNIQUE

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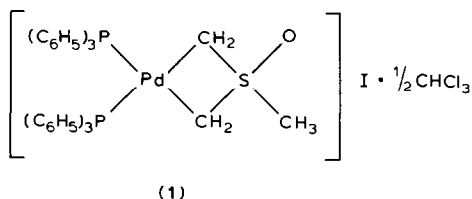
Summary

Reactions of $[\text{S}(\text{O})(\text{CH}_3)_3]\text{I}$ in NaOH solutions of various concentrations with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ in CHCl_3 in the presence of $n\text{-Bu}_4\text{NI}$ produced $[\text{Pd}(\text{PPh}_3)_2\text{-}\{(\text{CH}_2)_2\text{S}(\text{O})(\text{CH}_3)\}]\text{I} \cdot \frac{1}{2}\text{CHCl}_3$ (1), and $\text{Pd}(\text{PPh}_3)(\text{I})\{(\text{CH}_2)_2\text{S}(\text{O})(\text{CH}_3)\} \cdot \frac{1}{2}\text{CHCl}_3$ (2) with good yields. Without the phase transfer catalyst, no ylide complexes were formed. Compounds 1, 2, and the ionic compounds *cis*- $[\text{Pd}(\text{PPh}_3)_2\{(\text{CH}_2)\text{S}(\text{O})(\text{CH}_3)_2\}_2]\text{I}_2$ (3) were also prepared with low yields by the reaction of the ylide $(\text{CH}_2)\text{S}(\text{O})(\text{CH}_3)_2$ with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ in dry THF under an inert atmosphere. The advantages of phase transfer technique are discussed.

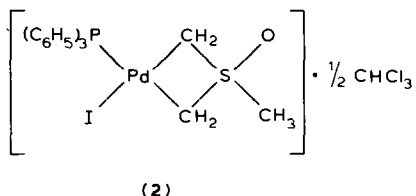
Phase transfer catalysis has become a useful technique for conducting synthetic reactions in heterogeneous media [1]. Numerous papers have been published since Jarrouse [2] in 1951 observed that quaternary ammonium salts markedly accelerated the two-phase reaction of benzyl chloride with cyclohexane. Examples of the application of phase transfer catalysis (PTC) to organometallic synthesis have also been reported [3]. Although phase transfer catalyzed reactions of sulfur ylides with aldehydes have been described in the literature [4], the preparation of metal ylide complexes by the PTC technique has not yet been reported. Sulfur ylide metal complexes were normally prepared in a homogeneous organic solvent under rigorous conditions [5]. In this paper we wish to report the use of phase transfer catalysis as a simple and convenient method for the preparation of palladium sulfur ylide compounds.

Trimethyloxosulfonium iodide (1.78 mmol) in 10 ml of 2.5 N NaOH was stirred for 1 h, then $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.71 mmol) and $n\text{-Bu}_4\text{NI}$ (0.13 g) in CHCl_3 (35 ml) were added. The organic layer turned from light yellow to orange red and became then colorless. The organic layer after work-up afforded a white

solid (> 60% yield). If the ether 18-crown-6 was used instead of $n\text{-Bu}_4\text{NI}$ as the phase transfer catalyst the reaction rate increased. In the absence of $n\text{-Bu}_4\text{NI}$ no ylide complex was formed. The white solid was proved to be $[\text{Pd}(\text{PPh}_3)_2\{(\text{CH}_2)_2\text{S}(\text{O})(\text{CH}_3)\}] \text{I} \cdot \frac{1}{2}\text{CHCl}_3$ (1). Anal. Found: C, 53.33; H, 4.32. $\text{C}_{39}\text{H}_{37}\text{IOP}_2\text{PdS} \cdot \frac{1}{2}\text{CHCl}_3$ calcd.: C, 53.10; H, 4.24%. IR, $\nu(\text{SO})$ 1190 cm^{-1} . λ_M DMSO was 36 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. ^1H NMR spectrum showed phenyl protons around 7–8 ppm, triplet methyl protons at 3.35 ppm, and an AA'BB' like methylene signal from 1.95 to 2.78 ppm. The pattern of methyl and methylene signal is similar to that of Bravo's $[\text{Pd}(\mu\text{-I})\{(\text{CH}_2)_2\text{S}(\text{O})(\text{CH}_3)\}]_2$ [6] which contains a chelated sulfur ylide.



When 10 ml of 0.2 N NaOH was used instead, the organic layer turned orange and then light yellow. After work-up a light yellow solid $\text{Pd}(\text{PPh}_3)(\text{I})\{(\text{CH}_2)_2\text{S}(\text{O})(\text{CH}_3)\} \cdot \frac{1}{2}\text{CHCl}_3$ (2) was obtained in > 60% yield. Anal. Found: C, 41.10; H, 3.68; I, 20.34. $\text{C}_{21}\text{H}_{22}\text{IOPPd} \cdot \frac{1}{2}\text{CHCl}_3$ calcd.: C, 40.96; H, 3.61; I, 20.13%. IR: $\nu(\text{SO})$ 1180 cm^{-1} . The ^1H NMR spectrum showed phenyl protons around 7–8 ppm, a triplet methyl signal at 3.25 ppm, and a complicated methylene signal from 1.95 to 2.28 ppm. The pattern is assigned to a bidentate sulfur ylide anion with 4 nonequivalent methylene protons.

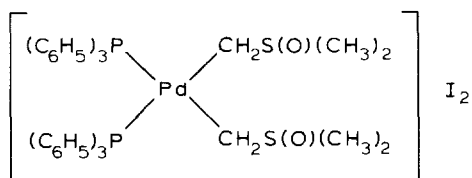


Both 1 and 2 are bidentate oxosulfonium ylide [7] presumably through transylidation [8]. In CHCl_3 2 was converted slowly to 1 at room temperature. The reasons for formation of 1 and 2 at different NaOH concentrations are not clear, but may be explained by the equilibrium of OH^- and I^- anions in the organic phase. Formation of 2 is preferred by the higher concentration of I^- in the organic phase, so that I^- may displace the coordinated PPh_3 , and formation of 1 is favored by the higher concentration of $n\text{-Bu}_4\text{NOH}$ in the organic layer, so that the interaction of 1 with $n\text{-BuNOH}$ increases the stability of 1 in the organic phase.

In order to compare a nonaqueous system with the phase transfer catalyzed two-phase system, we have carried out the reaction in THF under rigorous conditions. $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ in dry THF under N_2 was treated with two equivalents of oxosulfonium ylide (by treating trimethyloxosulfonium iodide with NaH for 24 h followed by titration to determine the amount of ylide formed). After work-up, three different compounds were identified: 1, 2 and $[\text{Pd}(\text{PPh}_3)_2\text{-}$

$\{(\text{CH}_2\text{S}(\text{O})(\text{CH}_3)_2)\}_2\text{I}_2$ (3) which contains two *cis* monodentate oxosulfonium ylides. Compound 3 was characterized as follows: ^1H NMR, a singlet methyl signal at 3.25 ppm and a doublet methylene signal at 2.80 ppm, $^3\text{J}(\text{CH}_2\text{PdP})$ 10 Hz, relative intensity 3/1. λ_M $80 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMSO. Anal. Found: C, 46.86; H, 4.32. $\text{C}_{42}\text{H}_{46}\text{I}_2\text{O}_2\text{P}_2\text{PdS}_2$ calcd.: C, 47.18; H, 4.31%. IR, $\nu(\text{SO})$ 1203 cm^{-1} . The yields of these three compounds were poor ($\sim 10\%$ each) and the separation of 1 and 2 was difficult. Changing the molar ratio of ylide to $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ did not significantly improve the yield. On the other hand, the phase transfer catalysis technique gave good isolated yields of 1 and 2.

The high yields, no need for the separation process, use of NaOH rather than NaH as the base, a process using only simple glassware and ambient, rather than rigorous, conditions certainly favor the phase transfer catalysis technique. We hope this communication will stimulate the use of this technique in the preparation of ylidemetal complexes.



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References

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