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PREPARATION OF SULFONIUM- η^3 -ALLYLIDE COMPLEXES
OF PALLADIUM(II)

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Summary

New palladium(II) complexes containing dimethylsulfonium allylide and tetramethylenesulfonium allylide as η^3 -allyl- ligands were prepared by treatment of the corresponding allyl-sulfonium salt and palladium bromide with sodium acetate. Thermally unstable sulfonium allylides were readily captured on a palladium metal by this straightforward preparation. Spectroscopic results of these new complexes were also discussed.

Introduction

A straightforward preparation of 1-trialkylphosphonium- η^3 -allylide complexes of dihalogenopalladate(II)¹⁾ was extended to the preparation of stabilized phosphonium ylide complexes bearing electron-withdrawing substituents at the ylidic carbon

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atom²⁾. This preparation of ylide complexes, although it has some limitation, is superior to former syntheses^{5,6)}.

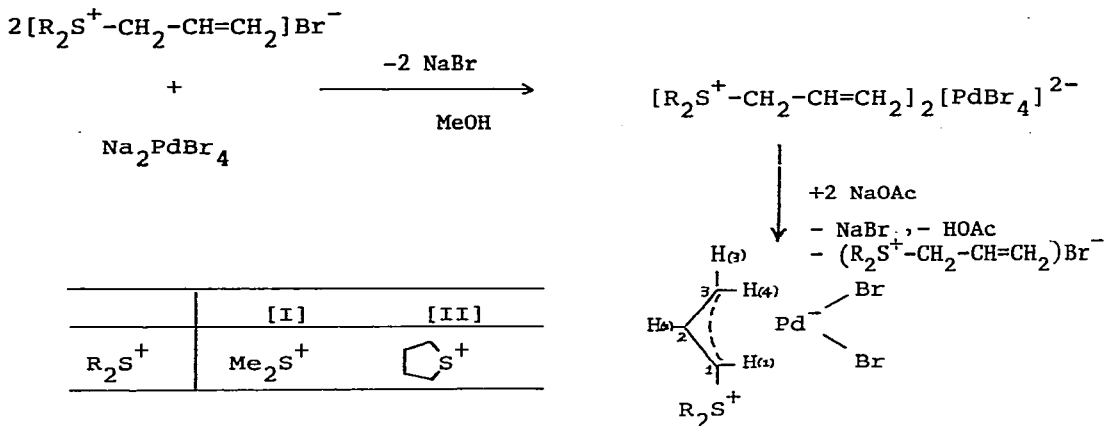
The chemistry of transition-metal complexes with coordinated phosphorus or sulfur ylides have been investigated in recent years⁴⁾. Included among these is a triphenylphosphonium cyclopentadienylide complex of tetrakis-(methoxycarbonyl)palladiacyclopentadiene; (Cpylid) [PdC₄(CO₂Me)₄]³⁾, in which Cpylid was a η^3 -allyl ligand.

This paper describes some new sulfonium allylide complexes of dibromopalladate(II) which were prepared by an extended onium salt method originally developed in these laboratories by the present author^{1,2)}.

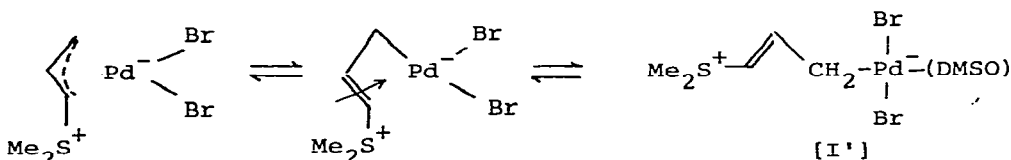
Results and Discussion

The 1-triphenylphosphonium- η^3 -allylide complexes previously reported¹⁾ exhibited complex allyl patterns in these NMR spectra because of coupling between the phosphorus atom and the allylic protons. In order to obtain more detailed information and to extend our procedure to other ylidic systems, we have taken two sulfonium allylides as ligands to the palladium atom. Sulfonium allylides are reported to be more highly labile than phosphonium ylides and often readily induce a Stevens type rearrangement⁷⁾. Therefore, the common ligand exchange process is inadequate.

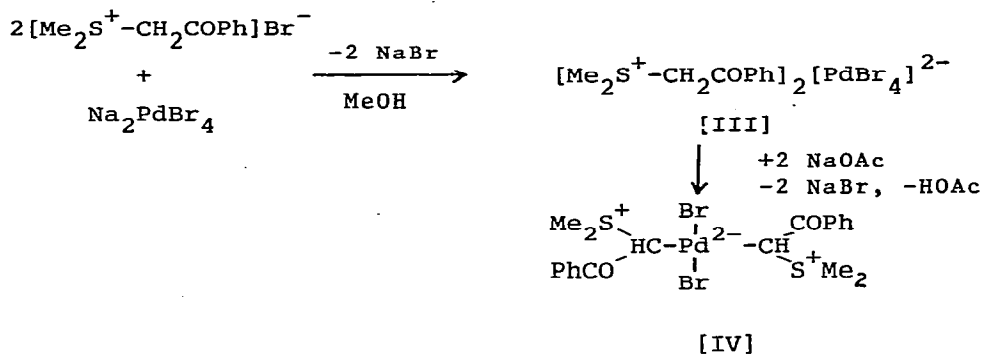
When allyl dimethylsulfonium or allyl tetramethylenesulfonium bromide was treated with disodium tetrabromopalladate in methanol at room temperature, the corresponding bis(allylsulfonium)tetrabromopalladate formed instantaneously. Sodium acetate then was added to the mixture at room temperature. Dimethylsulfonium- η^3 -allylide dibromopalladate(II) [I] and tetramethylenesulfonium- η^3 -allylide dibromopalladate(II) [II] were thus formed in 68 and 79 % yield, respectively.



Infrared spectrum of [I] in solid state exhibited characteristic ν_s and ν_{as} (C-C-C) stretching frequencies of the η^3 -allyl structure at 1475(w) and 1040(vs) cm^{-1} , respectively, which were comparable to the absorptions at 1490(w) and 1200(vs) cm^{-1} of $[(\eta^3\text{-allyl})\text{PdBr}]_2^{8)}$. The NMR spectrum in DMSO- d_6 of [I] is similar to that of 1-triphenylphosphonium- η^3 -allylide dibromopalladate¹⁾, showing two protons at the C(3) carbon atom; H(3) and H(4) were equivalent. A broad doublet at δ 4.52 for H(1) and an apparent quartet at δ 6.08 for H(2) were consistent with the view that the allylic part of the allylide ligand exhibited a strong interaction with the palladium atom at the C(3) position. The broad doublet signal of H(3) and H(4) became sharpened on raising the temperature. However, this change did not affect the other signals of the allylide resonance. This phenomenon was explained in terms of a dynamic allyl structure interacting at the C(3) position, [I']. Thermal decomposition of [I] occurred at 70°C in DMSO- d_6 give coordinated dimethylsulfide and 1,3,5-hexatriene.



Present method is easily applied to the synthesis of a stabilized sulfonium ylide complex which had been prepared previously by a ligand exchange process⁵⁾. In contrast to the formation of a binuclear complex of the one to one ylide-palladium adduct in the case of stabilized phosphonium ylides²⁾, the stabilized sulfonium ylide gave a monomeric palladium complex containing two ylidic ligands.



Experimental

Infrared spectra were measured on a JASCO DS-403G spectrometer in KBr disks. NMR spectra were recorded on a JEOL C-60HL spectrometer using tetramethylsilane as an internal standard. Starting sulfonium bromides were prepared by the reaction of dimethyl sulfide, tetramethylene sulfide and allyl bromide. The preparation of complexes [I]~[IV] was achieved without any precautions to exclude moisture or oxygen in the air unless noted otherwise.

Dimethylsulfonium- η^3 -allylide dibromopalladate(II) [I]

To a methanol (10 ml) solution of dimethylallylsulfonium bromide (1.0 g; weighing was performed under nitrogen because of its hygroscopicity), a methanol (15 ml) solution of Na_2PdBr_4 (1.84 g; 4.0 mmol) was added with stirring at room temperature. A brown precipitate of dimethylallylsulfonium tetrabromopalladate was formed instantaneously. A methanol (10 ml) solution of sodium acetate

(361 mg; 4.4 mmol) was added to the above suspension with vigorous stirring for 10 hr at room temperature. The color of precipitate changed gradually to yellow. The yellow precipitate were collected by filtration and washed with methanol to eliminate dimethylallylsulfonium bromide, giving [I] (986 mg) in 68 % yield. Recrystallization from a large volume of acetonitrile afforded small platelets, mp 170 °C (dec). (Found: C, 16.46; H, 2.75. $C_5H_{10}SBr_2Pd$ calcd.: C, 16.30; H, 2.74 %). 1H -NMR (DMSO- d_6) δ 6.08 (q, 1H, C(2)H, $J_{C(2)H-C(1)H} = 9.0$, $J_{C(2)H-C(3)H} = 9.0$ Hz), 4.51 (d, 1H, C(1)H), 3.95 (d, 2H, C(3)H₂), 3.18 (s, 6H, SCH₃) ppm.

Tetramethylenesulfonium- η^3 -allylide dibromopalladate (II) [II]

By a similar way was prepared [II] in 79 % yield (830 mg) from tetramethyleneallylsulfonium bromide (1.0 g; 5 mmol in 10 ml of methanol), Na₂PdBr₄ (1.27 g; 2.7 mmol in 15 ml of methanol), and sodium acetate (240 mg; 3.0 mmol in 10 ml of methanol), mp 159~161 °C (dec). (Found: C, 21.35; H, 3.22. $C_7H_{12}SBr_2Pd$ calcd.: C, 21.32; H, 3.06 %). 1H -NMR (DMSO- d_6) δ 6.06 (q, 1H, C(2)H, $J_{C(2)H-C(1)H} = 9.0$ Hz, $J_{C(2)H-C(3)H} = 9.0$ Hz), 4.82 (d, 1H, C(1)H), 4.03 (d, 2H, C(3)H₂), 3.80 (s, 4H, SCH₂), 2.30 (s, 4H, SC-CH₂) ppm. The starting sulfonium salt could be handled in air.

Bis(phenacyldimethylsulfonium)tetrabromopalladate (II) [III]

A methanol (5 ml) solution of phenacyldimethylsulfonium bromide (516 mg; 2.0 mmol) was added dropwise to a stirred methanol (10 ml) solution of disodium tetrabromopalladate (477 mg; 1.0 mmol). Reaction occurred instantaneously to give a pale-brown crystalline product, which was separated by filtration and washed with a large volume of water. Bis(phenacyldimethylsulfonium)tetrabromopalladate [III] was isolated quantitatively (852 mg), mp 175.0~175.8 °C. (Found: C, 30.16; H, 3.40. $C_{20}H_{26}O_2S_2Br_4Pd$ calcd.: C, 30.46; H, 3.32 %).

IR(KBr) $\nu(\text{CO})$, 1675 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6) δ 8.0~7.5 (m, 5H, C_6H_5), 5.60 (s, 2H, SCH_2), 3.10 (s, 6H, SCH_3) ppm.

Bis(dimethylsulfonium phenacylide)dibromopalladate(II) [IV]

To a methanol (10 ml) suspension of [III] (470 mg; 0.6 mmol) was added dropwise a methanol (5 ml) solution of sodium acetate (100 mg; 1.2 mmol) with vigorous stirring. The mixture was stirred for 4 hr at room temperature. The color of the precipitate changed gradually from pale-brown to yellow. Bis(dimethylsulfonium phenacylide)dibromopalladate [IV] was isolated in quantitative yield (400 mg), mp 240 °C (dec). (Found: C, 38.17; H, 3.91. $\text{C}_{20}\text{H}_{24}\text{O}_2\text{S}_2\text{Br}_2\text{Pd}$ calcd.: C, 38.33; H, 3.86 %). IR(KBr) $\nu(\text{CO})$, 1620 cm^{-1} , $^1\text{H-NMR}$ (DMSO- d_6) δ 8.1~7.3 (m, 5H, C_6H_5), 5.22 (s, 2H, SCH), 2.76, 2.65, 2.53 (three singlets, 6H, CH_3S) ppm.

[IV] also was directly prepared in quantitative yield from dimethylphenacylsulfonium bromide and disodium tetrabromopalladate with sodium acetate using the procedure described for [I].

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