

Note

# The first chelating olefin: Solid-state structure of *bis*-( $\eta^1$ -4-phenyl- $\eta^2$ -1-butene)silver (I) tetrafluoroborate

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## Abstract

A complex of 4-phenyl-1-butene with silver ion has been prepared by mixing silver (I) tetrafluoroborate with the neat ligand at room temperature. Purification by crystallization produces a stable complex characterized by solid-state structure. The *bis*-( $\eta^1$ -4-phenyl- $\eta^2$ -1-butene)silver (I) tetrafluoroborate complex contains a pair of olefin ligands that chelate a single silver atom *via* both olefin and aromatic Ag–C bonds. This is the first chelated organometallic silver complex reported in the literature assembled with only Ag–C bonds. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Silver; Olefin; 4-Phenyl-1-butene; Chelate; Silver–carbon bond; Structure

## 1. Introduction

It is well known that silver forms complexes with unsaturated groups, present either as olefins or as aromatic rings [1–12]. Many of these tend to be unstable solids or transient species within polymer membranes used as olefin separation devices. A good example is the silver–olefin/aromatic bonding in the complex observed in the silver coordination polymer of 1,8-diphenylocta-1,3,5,7-tetraene [13]. In this case, normal Ag–olefin and Ag–aromatic Ag–C bonds are observed, although the ability to isolate a complex was dependent on the anion used. The ability to prepare silver–olefin complexes having improved stability yet containing only Ag–C bonds could provide a better understanding of silver ion moderated olefin transport properties and another route to new materials.

A new class of silver–olefin complexes seems to be developing in recent literature reports in which various donor components of the ligand act in concert in a chelating mode, much as in well-established silver coordination chemistry

having ligands containing suitably positioned heteroatom donors [14,15]. In these recent organometallic cases, however, half of the chelate ligand comprises heteroatom donors, so these are not exclusively olefin-based chelate ligands. However, we have discovered that 4-phenyl-1-butene, Fig. 1, is capable of functioning as a completely olefin chelate for Ag<sup>+</sup>, which reacts under ambient conditions to form a stable, *bis*-chelated silver complex having a 2:1 ratio of ligand:Ag<sup>+</sup>.

The 4-phenyl-1-butene complex with silver, *bis*-( $\eta^1$ -4-phenyl- $\eta^2$ -1-butene)silver (I) tetrafluoroborate, is sufficiently stable to isolate and characterize. It is stable for months under laboratory storage conditions (minimal light exposure) and only slowly loses the ligand by dissociation/evaporation. The details of the preparation and crystal structure characterization of this complex are reported below.

## 2. Results and discussion

We have continued investigating silver coordination chemistry involving heteroatom ligands, which are important for imaging applications [16,17]. There is a rich variety of complexing modes ranging from relatively simple

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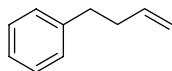


Fig. 1. 4-Phenyl-1-butene.

dimeric monomers that exhibit good water solubility [18,19] to complexes having particularly poor solubility [20,21]. In most cases, extensive inter-complex bonding between the silver atom and various donor atoms tend to facilitate the formation of extended networks resulting in multidimensional coordination polymers, which become difficult to redissolve in non-coordinating solvents. Recently, when attempting to dissolve  $\text{AgBF}_4$  in neat 4-phenyl-1-butene, a high yield of an insoluble white complex formed, which could be isolated and easily redissolved in a variety of non-coordinating solvents. On recrystallization, the structure of the *bis*-( $\eta^1$ -4-phenyl- $\eta^2$ -1-butene)silver (I) tetrafluoroborate complex was found to comprise two organic ligands bound to the silver by Ag–C bonds from both the olefin and the aromatic ring, and a coordinatively

isolated  $\text{BF}_4^-$  anion, as shown in the ORTEP diagram for the structure (Fig. 2). However, the crystal structure of the complex may be somewhat stabilized by weak interactions between the hydrogen atoms on the ligand and the F atoms on the  $\text{BF}_4^-$  counterion (Table 1). The unit cell packing pattern in *bis*-( $\eta^1$ -4-phenyl- $\eta^2$ -1-butene)silver (I) tetrafluoroborate shows a discreet placement of the complex with the  $\text{BF}_4^-$  anion in cavities formed between neighboring olefin complexes.

While silver–olefin complexation is well known in the literature, their characterization by solid-state X-ray diffraction has been hampered by limited stabilities. The *bis*-( $\eta^1$ -4-phenyl- $\eta^2$ -1-butene)silver (I) tetrafluoroborate complex, however, is unusually stable by comparison, although it can be observed to slowly darken over time (months in the dark). Normal Ag–C bonds in silver–olefin complexes range from 2.35 to 2.70 Å, with the average being around 2.6 Å. The Ag–C bonds in the title complex are generally at the upper end of that range, Table 2. Viewing the Ag–olefin coordination as occupying a single coordination site, the silver is four-coordinate in this complex, which is

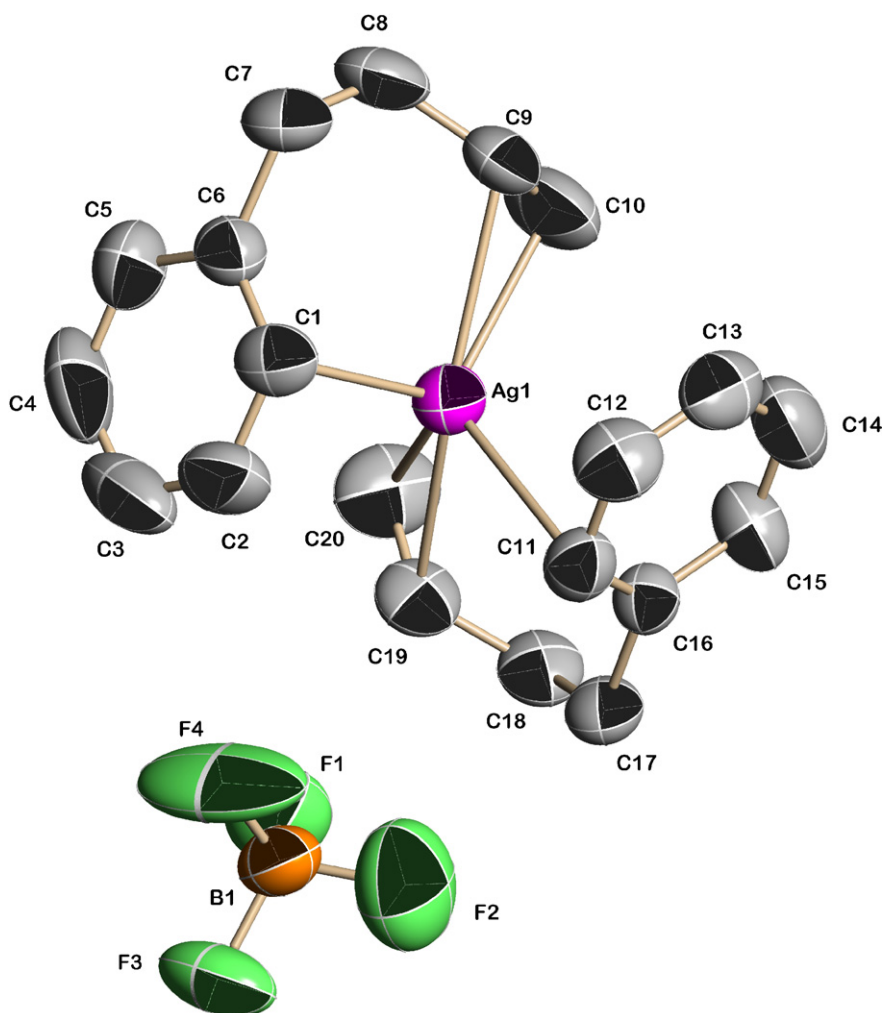


Fig. 2. ORTEP diagram of the title complex (with the atomic numbering scheme). Thermal ellipsoids were drawn at the 50% probability level for non-hydrogen atoms (hydrogen atoms are omitted for clarity).

Table 1  
Weak interactions between the hydrogen atoms on the ligand and the F atoms of the  $\text{BF}_4^-$  counterion

D–H...A	D–H	H–A	D–A	D–H–A
C(1)–H(1)–F(3)	0.98	2.55	3.468(8)	157
C(12)–H(12)–F(3)	0.93	2.48	3.312(9)	149
C(14)–H(14)–F(4)	0.93	2.43	3.348(12)	169

Table 2  
Selected Ag–C bond distances, Å, and angles, °, in *bis*-( $\eta^1$ -4-phenyl- $\eta^2$ -1-butene)silver (I) tetrafluoroborate and the polymeric silver complex with 1,8-diphenylocta-1,3,5,7-tetraene [13]

Title complex	Polymer complex		
Ag(1)–C(1) aromatic	2.547(6)	Ag(1)–C(2) aromatic	2.530(7)
Ag(1)–C(11) aromatic	2.692(5)	Ag(1)–C(3) aromatic	2.417(5)
Ag(1)–C(9)	2.546(7)	Ag(1)–C(9)	2.410(6)
Ag(1)–C(10)	2.401(7)	Ag(1)–C(10)	2.445(6)
Ag(1)–C(19)	2.566(6)		
Ag(1)–C(20)	2.408(6)	Ag(1)–O(1)	2.396(5)
		Ag(1)–O(3)	2.541(5)
C(8)–C(9)–C(10)	124.9(8)	C(8)–C(9)–C(10)	122.5(3)
C(1)–C(6)–C(7)	121.7(6)	C(1)–C(6)–C(7)	119.6(3)

common in silver coordination polymer chemistry [22], with a Ag–olefin midpoint bond distance of 2.37(1) Å. The resulting geometry around the silver is distorted tetrahedral.

The terminal carbons of the title complex ligand show the shortest Ag–C bond lengths at 2.401(7) Å, C(10), and 2.408(6) Å C(20), and the distance to the second carbon in this  $\eta^2$  bond is longer, at 2.546(7) and 2.566(6) Å, which are similar to the Ag–C olefin bonds of 2.410(6) and 2.445(6) Å in the silver coordination polymer of 1,8-diphenylocta-1,3,5,7-tetraene, Fig. 3 [13]. The ligand in this latter complex can be approximately considered as a dimer of 4-phenyl-1-butene and one half of it can be viewed in comparison to the *bis*-( $\eta^1$ -4-phenyl- $\eta^2$ -1-butene)silver (I) tetrafluoroborate complex reported here.

The Ag–C aromatic bond lengths are distinctly longer in the title compound, 2.547(6) and 2.692(5) Å, compared to those in the silver polymer complex, 2.417(5) and 2.530(7) Å. It should be noted that the Ag–C bonds are those involving the *ortho*-carbon in the title complex while they involve the *meta*- and *para*-carbons in the polymer.

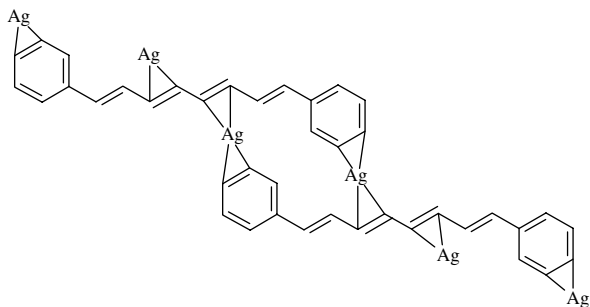


Fig. 3. Schematic of silver coordination with 1,8-diphenylocta-1,3,5,7-tetraene [13].

Considering the overall similarity between ligand components, it is curious that the 1,8-diphenylocta-1,3,5,7-tetraene ligand produces a polymer while the 4-phenyl-1-butene generates a monomeric complex. That is, based on the structure of the title complex, a monomeric complex of 1,8-diphenylocta-1,3,5,7-tetraene containing two silver ions would have been predicted. One factor that may be taken into account is that the  $\text{BF}_4^-$  anion is not significantly involved with the silver complexation in the title complex while the  $\text{ClO}_4^-$  anion clearly provides secondary silver bonding in the polymer, as shown by the Ag–O distances of 2.396(5) and 2.541(5) Å. In addition, the olefin and aromatic bond angles related to silver coordination in the title complex are slightly less constrained compared to the polymeric complex.

The most significant infrared marker is the moderately strong  $1640\text{ cm}^{-1}$  C=C stretch in the 4-phenyl-1-butene ligand that is clearly shifted to  $1591\text{ cm}^{-1}$ . This  $49\text{ cm}^{-1}$  shift is attributed to significant  $\pi$ -back bonding upon complexation, and is consistent with similar complexes reported elsewhere [1,14,23,24].

We have also attempted the preparation of analogous complexes with  $\text{AgNO}_3$ ,  $\text{AgO}_2\text{CCF}_3$ , and  $\text{AgO}_2\text{CCH}_3$ , with success in the isolation of a stable product decreasing in that order and none as stable as the  $\text{BF}_4^-$  complex. This is similar to the observations made with the silver 1,8-diphenylocta-1,3,5,7-tetraene polymer complex [13] and is consistent with the observation of  $\text{Ag}^+$  reduction in polymers, where the reduction rate of silver ions strongly depended on the counter anions [25].

### 3. Experimental

#### 3.1. Preparation of *bis*-( $\eta^1$ -4-phenyl- $\eta^2$ -1-butene)silver (I) tetrafluoroborate

Preparation of *bis*-( $\eta^1$ -4-phenyl- $\eta^2$ -1-butene)silver (I) tetrafluoroborate: 1.0 g (5.1 mmol) of solid  $\text{AgBF}_4$  was added to 4.0 g (30 mmol) of 4-phenyl-1-butene (no other solvent). The thick white paste that formed was diluted with 5 mL toluene, stirred 2 h, filtered, washed with ether, and air dried. Crystals suitable for X-ray crystal structure determination were prepared by slowly evaporating a solution of 0.34 g of this complex in 10 mL of ethyl acetate at room temperature. Large, colorless plates were obtained. Differential Scanning Calorimetry (TA Instruments, DSC model 951) shows a sharp melting point endotherm centered at  $97.5\text{ }^\circ\text{C}$ . The title complex is not soluble in ether, is soluble in toluene, and is very soluble in acetone, acetonitrile, and ethyl acetate.  $\text{C}_{20}\text{H}_{24}\text{AgBF}_4$  Found (theory): C = 51.79 (52.33), H = 5.02 (5.27).

#### 3.2. X-ray structure determination

A crystal of approximate dimensions  $0.5 \times 0.5 \times 0.25\text{ mm}^3$  was chosen for data collection (150 K) using a Nonius Kappa-CCD [26] diffractometer. The unit cell for  $\text{AgBF}_4$  complex was determined to be orthorhombic and the space

Table 3

Crystal data and structure refinement for *bis*-( $\eta^1$ -4-phenyl- $\eta^2$ -1-butene)silver (I) tetrafluoroborate

Empirical formula	C <sub>20</sub> H <sub>24</sub> AgBF <sub>4</sub>
Formula weight	459.07
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	15.7383(6)
<i>b</i> (Å)	15.5703(6)
<i>c</i> (Å)	16.2819(8)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	3989.9(3)
<i>Z</i>	8
Density (calc.) (Mg/m <sup>3</sup> )	1.528
Absorption coefficient (mm <sup>-1</sup> )	1.046
<i>F</i> (000)	1856
Crystal size (mm <sup>3</sup> )	0.5 × 0.5 × 0.25
$\theta$ Range for data collection (°)	4.18–27.52
Index ranges	−19 ≤ <i>h</i> ≤ 20, −20 ≤ <i>k</i> ≤ 20, −21 ≤ <i>l</i> ≤ 17
Reflections collected	18 552
Independent reflections [ <i>R</i> (int)]	4539 [0.1545]
Completeness to $\theta = 27.52^\circ$	98.8%
Absorption correction	Multi-scan (SORTAV) [28]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	4539/0/236
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.901
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0566, <i>wR</i> <sub>2</sub> = 0.1161
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1872, <i>wR</i> <sub>2</sub> = 0.1514
Extinction coefficient	0.0127(7)
Largest difference of peak and hole (e Å <sup>-3</sup> )	0.472 and −0.534

group was uniquely determined from systematic absences to be *Pbca*. The structure was solved by direct methods and refined by full-matrix least-squares method with anisotropic displacement parameters for the non-hydrogen atoms using Bruker, SHELXTL [27] software. Hydrogen atoms were included in idealized positions with isotropic displacement parameters. Details of cell data, data collection, and structure refinement are summarized in Table 3.

### Acknowledgements

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### Appendix A. Supplementary material

CCDC 654186 contains the supplementary crystallographic data for this paper. These data can be obtained

free of charge via <http://www.ccdc.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.08.036](https://doi.org/10.1016/j.jorganchem.2007.08.036).

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