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SYNTHESIS AND PROPERTIES OF h^5-CYCLOPENTADIENYL(TRIPHENYLPHOSPHINE)SILVER(I)

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Summary

The title compound has been prepared by treatment of a solution of cyclopentadienylsodium and triphenylphosphine in tetrahydrofuran with a solution of silver trifluoromethanesulfonate ($AgSO_3CF_3$) in tetrahydrofuran. It decomposes slowly at room temperature, but can be stored indefinitely at —80° C. IR spectra indicate that a C_5H_5-h^5-group is present in the molecule and this conclusion is confirmed by ^1H and ^{13}C NMR spectroscopy.

Introduction

Cyclopentadienyl compounds of both copper and gold are known, e.g. $C_5H_5Cu^IP(C_2H_5)_3$ [1] and $C_5H_5Au^IP(C_6H_5)_3$ [2], but the synthesis of cyclopentadienylsilver derivatives has not been reported. The only previously known compounds which contain both silver and one or more cyclopentadienyl groups, are 1-(1^1-chloroferrocenyl)silver [3] and cyclopentadienylmanganese tricarbonylsilver [4]. We now describe the synthesis and characterization of the triphenylphosphine complex of h^5-C_5H_5Ag.

Experimental

General

All experiments were carried out under dry, oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled before use under nitrogen.

NMR spectra were recorded on Varian HA-100 and XL-100/15FT NMR spectrometers with DMF-d_7 as solvent.

The IR spectra were recorded on a Perkin—Elmer 457 grating infrared spectrometer using Nujol and polytrifluorochloroethylene mulls between KBr disks and Nujol mulls between CsI disks. Reported wavenumbers are believed to be accurate to ±3 cm^{-1}.

Elemental analyses were carried out under the supervision of Mr. W.J. Buis in the Analytical Department of the Institute for Organic Chemistry TNO at Utrecht.

(Cyclopentadienyl)triphenylphosphinesilver(I)

A solution of $AgSO_3CF_3$ (2.5 g; 10 mmol) in 50 ml of THF was added with stirring during 30 min to a solution of C_5H_5Na (0.9 g; 11 mmol) and $P(C_6H_5)_3$ (2.6 g; 10 mmol) in 50 ml of THF at —80° C. The initial pink colour of the solution gradually changed to red-brown and a white precipitate was formed. After the addition of the solution of the silver salt, the mixture was stirred for 4 h at —80° C. The supernatant red-brown solution was decanted off and the white precipitate was washed three times with 20 ml of THF and three times with 25 ml of pentane. In this way (cyclopentadienyl)triphenylphosphinesilver(I) was obtained after drying in vacuo (10^{-6} mmHg) at —20° C with a yield of 80%; (dec. temp. 75° C; analyses found: C, 63.57; H, 5.70; P, 6.42; $C_{23}H_{20}AgP$ calcd.: C, 63.49; H, 4.60; P, 7.12%) *.

Results

Physical and chemical properties

The reaction of $AgSO_3CF_3$ with C_5H_5Na in the presence of $P(C_6H_5)_3$ in THF affords the white diamagnetic complex $C_5H_5AgP(C_6H_5)_3$. It is very sensitive to moisture and is insoluble in apolar or weakly polar solvents such as ethers, pentane and benzene. It is, however, fairly soluble in coordinating solvents, such as pyridine, *N,N*-dimethylformamide and *N,N*-dimethylacetamide. At room temperature it decomposes slowly, in solution and in the solid state. The pure compound can be stored at —80° C without change, but decomposes within 10 seconds at 75° C.

Spectroscopic data

(i) NMR data. At 0° C the ^{1}H NMR spectrum of cyclopentadienyl(triphenylphosphine)silver(I) in DMF-d_7 shows a well-defined singlet at δ 5.97 ppm (downfield from TMS) due to the cyclopentadienyl ring protons and a complex pattern from the three phenyl groups of triphenylphosphine centered at δ 7.5 ppm. On cooling to —65° C the singlet of the cyclopentadienyl ring protons remains un-

TABLE 1

^{13}C NMR RESONANCE POSITIONS [a] OF THE PPh_3 PART OF (CYCLOPENTADIENYL)TRIPHENYLPHOSPHINESILVER(I)

Compound	C_1	C_2	C_3	C_4
PPh_3 [b]	137.2 (12) [c]	133.6 (20) [c]	128.3 (7) [c]	128.5 (0) [c]
$C_5H_5Ag \cdot PPh_3$	132.5 (25)	134.8 (16)	131.1 (8.5)	129.3 (0)

[a] In ppm downfield from TMS. [b] Values agree with those of ref. 5. [c] ( ) denotes $J(C—P)$ in Hz.

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* According to the NMR spectrum, the sample still contained a small amount of tetrahydrofuran. Silver could not be determined in the presence of phosphorus.

changed. The spectrum shows no absorptions due to methylenic hydrogens in the δ 3 ppm region.

The ^{13}C NMR spectra are temperature independent down to −65°C and show

TABLE 2

VIBRATIONAL FREQUENCIES FOR $C_5H_5Ag \cdot PPh_3$ [a] AND PPh_3

$C_5H_5Ag \cdot P(C_6H_5)_3$		Ph_3P	
Infrared	Raman	Infrared	Assignments
1587w	1585	1582m	$k\nu(CC)(a_1)$
1573w		1569 1566 }w	$l\nu(CC)(b_2)$
1481s	1480	1482s	$m\nu(CC)(a_1)$
1437s		1435 1429 }s	$n\nu(CC)(b_2)$
1418m			C—C-stretching, $\nu_{CC}(\pi\text{-}C_5)$
		1390w(br)	$2\nu(A_1)$
1332w		1337 1322 }w	$o\nu(CC)(b_2)$
1312w	~1290	1307 1297 }w	$w + i(B_2)$
1292w(br)		1280 1268 }w	$c\beta(CH)(b_2)$
1185w	1180	1179w	$a\beta(CH)(a_1)$
1160w	1153	1157 1152 }w	$c\beta(CH)(b_2)$
1098s	1094	1089m	qX-sens(a_1)
		1068 1065 }w	$d\beta(CH)(b_2)$
1028m	1025	1028m	$b\beta(CH)(a_1)$
1001m	999	997 993 }w	p ring(a_1)
995s(br)			CH in plane wagging C_5H_5
		985w	$j\gamma(CH)(b_1)$
		970w	$h\gamma(CH)(a_2)$
910	909	914 905 }w	$i\gamma(CH)(b_1)$
846w(br)	850	850	$g\gamma(CH)(a_2)$
		847	
820w(br)			CH out of plane wagging C_5H_5
755s(sh)	750	754	
750s		746	$f\gamma(CH)(b_1)$
745(sh)		741	
727vs(br)			CH out of plane wagging C_5H_5
710m	698	—	rX-sens(a_1)
695vs	692	695 692 }vs	$v\phi(CC)(b_1)$
620w	618	619w	$s\alpha(CCC)(b_2)$
		540w	
528		512	
517s	498	497	yX-sens(b_1)
504		489	
436m		433 423 }m	tX-sens(b_1)
	407w		
		~398	$w\Phi(CC)(a_2)$

[a] $C_5H_5Ag \cdot P(C_6H_5)_3$ decomposed in the laser beam.

one singlet at 103.2 ppm due to the carbon atoms of the cyclopentadienyl group. The resonances of the coordinated PPh_3 relative to those of the free ligand are listed in Table 1.

The high field shift for C_1 in the complex is caused by the partial donation of the lone pair on phosphorus to silver. A similar phenomenon has been observed for nitrogen ligands [6,7]. No long-range coupling of the cyclopentadienyl group with silver and phosphorus was observed.

The ^{31}P NMR spectrum, recorded at −65° C, consists of a broad doublet centered at 599 Hz downfield from triphenylphosphine. This is consistent with bonding between phosphorus and silver, in which d_π—d_π back bonding plays a very important role. Probably the doublet is caused by a phosphorus—silver coupling of at least 200 Hz. The considerable broadening of the doublet is consistent with ligand exchange at the cyclopentadienylsilver moiety.

(ii) Infrared data. The infrared spectral data of cyclopentadienyl(triphenylphosphine)silver(I) are reported in Table 2, together with those of triphenylphosphine [8].

The assignments of the bands due to internal vibrations of the triphenylphosphine part of the molecule are straightforward and were made by comparison with the spectrum of PPh_3 [8]. The spectra of the cyclopentadienylsilver compound contain several absorptions which are characteristic of coordinated PPh_3, viz. 1095s, 526s, 513s, 500m/s cm^{-1} (vibrational assignments are given by Deacon [8]). The spectra show (cf. Table 2) only a few absorptions due to internal vibrations of the cyclopentadienyl portion of the molecule, viz. 1418m, 995m, (br), 820w/m, 727s cm^{-1}. The C—H-stretching modes in the region 3100—3000 cm^{-1} are obscured by the stretching modes of the phenyl groups.

Discussion

The principal structural possibilities [9] (cf. Fig. 1) to be considered for C_5H_5-$Ag \cdot P(C_6H_5)_3$ are the π-bonded (*pentahapto*, A), the π-allyl (*trihapto*, B) and the σ-bonded (*monohapto*, C) structures.

Several examples are known in the literature of type A: e.g. $(C_5H_5)_2Fe$ [10] and $C_5H_5CuP(C_6H_5)_3$ [11] and of type C: e.g. $C_5H_5Au^{III}(CH_3)_2 \cdot P(C_6H_5)_3$ [12] and $(\sigma\text{-}C_5H_5)Fe(CO)_2(\pi\text{-}C_5H_5)$ [13]. A few arguments have been presented in favour of the occurrence of a *trihapto* structure, e.g. in $(C_5H_5)_3MoNo$ [14]. Real structural evidence for a h^3-structure was obtained for the aluminium compound $C_5H_5Al(CH_3)_2$ [15].

IR spectroscopy has been most extensively used to decide between the various

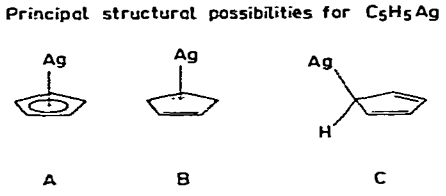

Fig. 1.

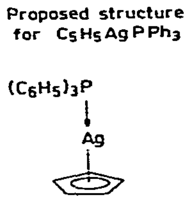

Fig. 2.

bonding modes of cyclopentadienyl groups. The criteria put forward by Cotton [16] and Nakamoto [17] proved very useful in deciding between a h^5 and a h^1 or h^3 structure. The IR spectra of (cyclopentadienyl)triphenylphosphinesilver(I) clearly show (cf. Table 2) the absorptions due to a h^5-C_5H_5 group, i.e. a very simple pattern in the 1500—250 cm^{-1} region (1418m, 995m, 820w and 727s cm^{-1}). The C—H stretching vibrations in the 3100—3000 cm^{-1} region are obscured by absorptions due to the phenyl groups of the triphenylphosphine.

The ^{1}H NMR spectra show a singlet for all the cyclopentadienyl protons; this is a necessary, but in itself insufficient argument for a π-type cyclopentadienyl ligand. The complex spectral pattern due to a σ-type structure may go undetected when there is a fast enough metal migration, resulting in the collaps of the complex pattern into a singlet. However, the spectra of (cyclopentadienyl)triphenylphosphinesilver(I) show no temperature dependence and no silver or phosphorus long-range coupling; this is in accordance with a π -structure in which the orbitals used for bonding have no σ-character.

The NMR and IR spectra (cf. Tables 1 and 2) show the presence of a metal-bonded triphenylphosphine group. The IR spectra are far too simple to be consistent with the presence of a *mono-* or *tri-hapto* cyclopentadienyl ring, but are in agreement with the expectations for a *pentahapto* ring. The NMR spectra are also consistent with a *pentahapto* cyclopentadienyl group. It thus appears, that silver(I), like copper(I), forms *pentahapto*-cyclopentadienyl derivatives, and therefore we propose for (cyclopentadienyl)triphenylphosphine silver(I) the structure shown in Fig. 2.

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