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THE REACTION OF DIARYLZINC COMPOUNDS WITH SILVER SALTS

SYNTHESIS AND CHARACTERIZATION OF ARYLSILVER(I) COMPOUNDS *

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Summary

The reaction of diarylzinc compounds with silver(I) salts is an excellent method of preparing stable arylsilver compounds in quantitative yields. These compounds have been characterized by IR and ^1H and ^{13}C NMR spectroscopy. Cryoscopy in benzene shows phenylsilver to be polymeric, and the methyl-substituted phenylsilver compounds to be trimers. All the compounds appear to be associated via aryl groups bridging between two silver atoms. As in the case of the corresponding copper compounds, the data point to the existence of rotation of these aryl groups around the C^1—C^4 axis.

Introduction

Although the first arylsilver compound, viz. $(PhAg)_2 \cdot AgNO_3$, was reported in 1919 [2], it was not until 1972 that pure phenylsilver was obtained [3]. It was described as a highly insoluble white compound of considerable thermal stability. Earlier attempts to prepare phenylsilver resulted in impure, thermally unstable products [4—6]. In all cases phenylsilver was contaminated with either magnesium, lithium, or silver salts. These contaminants were hard to remove and resulted in products of low thermal stability. Another complication was the partial reduction of the silver salts to metallic silver when organolithium or organomagnesium compounds were used as arylating agents. The organomagnesium route never led to pure, stable products. The organolithium route was succesful only in some special cases [7—9] in which it was possible to purify the products by extraction or recrystallization.

The method used by Beverwijk and Van der Kerk [3] employs trialkylaryl-

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* Part of this work was described in an earlier communication [1].

lead or -tin compounds as arylating agents. Although this route yields pure, stable arylsilver compounds of the type ArAg, it is cumbersome and restricted to small scale preparations (1 g) because of the special reaction conditions required. It was found that the problems mentioned above are eliminated completely when diarylzinc compounds are used as arylating agents.

Results and discussion

Synthesis of arylsilver compounds

When finely divided solid silver nitrate is stirred with a diethyl ether solution of diarylzinc compounds in excess (preferably in a 1/2 molar ratio) for more than 2 h at temperatures below 0°C the corresponding arylsilver compounds are formed as colourless solids in quantitative yields:

$$Ar_2Zn + AgNO_3 \rightarrow ArAg + [ArZnNO_3]$$

Ar = phenyl (I), 2-methylphenyl (II), 3-methylphenyl (III), 4-methylphenyl (IV) and 2,6-dimethylphenyl (V).

After washing with ether and pentane and drying in vacuo at —10°C the compounds were obtained analytically pure. Some analytical data of the arylsilver compounds thus prepared are summarized in Table 1.

The same reaction was also carried out with ether-soluble silver trifluoromethane sulphonate, $AgSO_3CF_3$, and with silver tetrafluoroborate, $AgBF_4$, and resulted in pure products only when the reaction temperature was kept below —30°C. Above —30°C, in the case of $AgBF_4$ the IR spectrum of the products obtained showed absorptions which must be attributed to tetraarylboride species formed by arylation of the anion. However, at —30°C or below pure arylsilver compounds were isolated in both cases.

After the addition of the silver salt to the diethyl ether solution of the diarylzinc compound transient, coloured intermediates are formed. These intermediates are complexes of the type $(ArAg)_n \cdot (AgX)_m$. From the reaction of diphenylzinc with silver nitrate an orange compound, analyzing as $PhAg \cdot (AgNO_3)_2$ was isolated in low yield. The stoichiometry of this complex is different from that

TABLE 1

SOME ANALYTICAL AND PHYSICAL DATA FOR ARYLSILVER COMPOUNDS

Compound ArAg Ar =	Decomposition temperature[a] (°C)	Molecular weight[b] (found (calcd.))	Degree of association	Analysis (Ag%) (found (calcd.))
Phenyl (I)	74	>2000 (185.0)	>10	58.1 (58.32)
2-Methylphenyl (II)	91	592 (199.0)	2.97	54.0 (54.22)
3-Methylphenyl (III)	82	600 (199.0)	3.01	53.2 (54.22)
4-Methylphenyl (IV)	78	615 (199.0)	3.08	53.7 (54.22)
2,6-Dimethylphenyl (V)	170	650 (213.0)	3.05	49.9 (50.66)

[a] The decomposition temperatures were determined by DTA at a heating rate of 5°C/min. [b] Molecular weights were determined by cryoscopy in benzene.

of the product obtained by Beverwijk using the aryl-lead or -tin reagents [10], viz. $(PhAg)_5 \cdot (AgNO_3)_2$.

In the further course of the reaction the colour disappears; apparently, the intermediate complexes are quickly arylated further by the diarylzinc compounds, in contrast to what happens in the corresponding reactions of phenyltin and -lead compounds, which require up to a thirty-fold excess of the arylating agent to give phenylsilver. The following reaction scheme is proposed:

$$\begin{array}{l} n\ \mathrm{Ar_2Zn} + (n+m)\ \mathrm{AgX} \rightarrow (\mathrm{ArAg})_n \cdot (\mathrm{AgX})_m + n[\mathrm{ArZnX}] \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow {\scriptstyle m\ \mathrm{Ar_2Zn}} \\ \qquad\qquad\qquad\qquad\qquad (n+m)\mathrm{ArAg} + m[\mathrm{ArZnX}] \end{array}$$

Physical and chemical properties of arylsilver compounds

Arylsilver compounds of the type ArAg are colourless solids, which are virtually insoluble in aliphatic solvents such as pentane and hexane. Phenylsilver is only slightly soluble in aromatic solvents and somewhat more soluble in chloroform and strongly coordinating solvents such as pyridine. The methyl-substituted arylsilver compounds are more soluble; they dissolve sufficiently in benzene to allow reliable measurements of their molecular weights to be made (cf. Table 1).

Arylsilver compounds are not very sensitive towards oxygen and moisture. The *ortho*-substituted compounds are less sensitive than the other derivatives, probably because of steric effects. The compounds are only slightly sensitive to light. After exposure to diffuse daylight for several days only traces of decomposition products are present. At room temperature all the compounds decompose slowly. The decomposition temperatures shown in Table 1 were measured by DTA at a heating rate of 5°C/min. It is apparent that the thermal stability rises considerably with the degree of *ortho*-methyl substitution. This *ortho*-effect has also been observed for the corresponding arylcopper compounds and is also well-known with organometallic compounds of transition metals. The decomposition temperatures of the arylsilver compounds are lower than those reported for the corresponding arylcopper compounds [11], so the latter are the more thermostable. The products of the thermal decomposition of solid arylsilver compounds are exclusively metallic silver and biaryls in which the newly formed carbon—carbon bond occupies the same ring position as the original silver—carbon bonds. (Analogous behaviour was previously noted for the corresponding copper compounds.) This type of decomposition, binuclear elimination, is well-known for organocopper, -silver, and -gold compounds [12]. It implies that the cleavage of Ag—C bonds and the formation of C—C bonds are synchronous processes which take place within the cluster compound without the participation of free radical intermediates or hydrogen transfer to the metal.

Cryoscopic molecular weight determinations in benzene showed phenylsilver, like phenylcopper, to be polymeric ($n > 10$). On the other hand, unlike the methyl-substituted arylcopper compounds which are tetramers, the corresponding methyl-substituted arylsilver compounds are all trimers. All molecular weights were found to be concentration independent.

In the course of this work, we also prepared 3-methylphenylcopper and 4-methylphenylcopper, which were not included in our earlier paper on arylcopper compounds [11]; both compounds were found to be non-dissociating tetramers in benzene.

Characterization of the arylsilver compounds

The IR spectra of phenylsilver are identical with those reported by Beverwijk [3]. In this paper only those IR absorptions of arylsilver compounds will be discussed which are believed to be associated with the substituents at the aromatic nucleus, as well as those which are characteristic for the ring-substitution pattern. The relevant data are presented in Table 2.

The spectra show the expected ring-substitution pattern which is indicated by the absorptions in the 700—800 cm^{-1} region (Table 2) and the 1650—2000 cm^{-1} region. Characteristic absorptions around 450, 670 and 1050 cm^{-1} are present also and are ascribed to vibration modes in which the silver substituent moves with appreciable amplitude. The Raman spectra of the arylsilver compounds show no absorptions in the region where silver—silver vibrations are expected (around 200 cm^{-1}). Thus, it is concluded that there is no silver—silver bonding in these multinuclear silver compounds.

The NMR spectral data presented in Table 3 show the same features as observed for the corresponding arylcopper compounds [11]. Relative to the parent hydrocarbons, the protons, carbon atoms and the methyl groups *ortho* to the metal are shifted to low field, whereas the protons and the carbon atoms in *meta* and *para* positions are not significantly shifted.

The ^1H NMR spectra show no Ag—^1H couplings and no Ag—^{13}C couplings are observed in the ^{13}C NMR spectra. No signals attributable to the silver-substituted carbon atom were detected. This may be due to exchange broadening of the signal, which would not in any case be of high intensity because of the lack of NOE enhancement and splitting as a result of ^{107}Ag—^{13}C and ^{109}Ag—^{13}C couplings. The absence of ^1H—Ag and ^{13}C—Ag couplings in the absorptions of the *ortho*-protons or -carbons, respectively, even at —95°C, indicates that the exchange is very fast. The exchange must be intramolecular since no concentration dependence was observed in the spectra.

In our earlier paper [11], four possible structures for arylcopper compounds were considered. Similar structures may occur for the corresponding arylsilver compounds, viz. one with aryl groups bridging between two silver atoms, a

TABLE 2

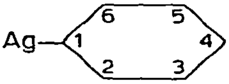
X-SENSITIVE VIBRATION MODES AND C—H OUT-OF-PLANE DEFORMATIONS OF ARYLSILVER COMPOUNDS

Compound ArAg Ar =	Assignments [a]				
	X-sensitive			γ(C—H)	
	q	*r*	*y*		
Phenyl (I)	1060m	676w	443s	724s	707s
2-Methylphenyl (II)	1030 [b]	670vw	438s	742vs	
3-Methylphenyl (III)	1040 [b]	668w	432s	765vs	709s
4-Methylphenyl (IV)	1030 [b]	600vw	n.o. [c]	783vs	
2,6-Dimethylphenyl (V)	1030 [b]	670vw	459s	774vs	708m

[a] Notation according to Refs. 13, 14. [b] Obscured by the rocking mode of the methyl group. [c] Not observed.

TABLE 3

^{1}H AND ^{13}C NMR SPECTRAL DATA [a] FOR ARYLSILVER COMPOUNDS AT −10°C IN $CDCl_3$ AND OF THE PARENT HYDROCARBONS



^{1}H NMR *spectra*

Compound ArAg Ar =	H^{1}	H^{2}	H^{3}	H^{4}	H^{5}	H^{6}	H(CH_3)
Phenyl (I)	—	7.78	7.3 [b]	7.3 [b]	7.3 [b]	7.78	—
Benzene	7.38	7.38	7.38	7.38	7.38	7.38	—
2-Methylphenyl (II)	—	—	7.2 [b]	7.2 [b]	7.2 [b]	7.79	2.80
Toluene	7.2 [b]	—	7.2 [b]	7.2 [b]	7.2 [b]	7.2 [b]	2.28
3-Methylphenyl (III)	—	7.63	—	7.2 [b]	7.2 [b]	7.61	2.26
Toluene	7.2 [b]	7.2 [b]	—	7.2 [b]	7.2 [b]	7.2 [b]	2.28
4-Methylphenyl (IV)	—	7.77	7.14	—	7.14	7.77	2.29
Toluene	7.2 [b]	7.2 [b]	7.2 [b]	—	7.2 [b]	7.2 [b]	2.28
2,6-Dimethylphenyl (V)	—	—	7.1 [b]	7.1 [b]	7.1 [b]	7.1 [b]	2.80
1,3-Xylene	7.0 [b]	—	7.0 [b]	7.0 [b]	7.0 [b]	—	2.29

^{13}C NMR spectra

Compound ArAg Ar =	C^{1}	C^{2}	C^{3}	C^{4}	C^{5}	C^{6}	C(CH_3)
Phenyl (I)	[c]	146.44	127.31	131.18	127.31	146.44	—
Benzene	128.69	128.69	128.69	128.69	128.69	128.69	—
2-Methylphenyl (II)	[c]	154.60	127.31	130.74	123.92	146.0(br)	30.23
Toluene	129.41	137.58	129.41	128.63	125.82	128.63	21.35
3-Methylphenyl (III)	[c]	146.94	136.26	131.90	126.84	143.23	21.40
Toluene	128.63	129.41	137.58	129.41	128.63	125.82	21.35
4-Methylphenyl (IV)	[c]	146.17	128.07	141.20	128.07	146.17	21.53
Toluene	125.82	128.63	129.41	137.58	129.41	128.63	21.35
2,6-Dimethylphenyl (V)	[c]	154.61	124.40	130.52	124.40	154.61	30.00
1,3-Xylene	129.61	137.21	125.84	127.88	125.84	137.21	20.86

[a] Chemical shifts were measured relative to internal TMS. [b] Mean value of a multiplet. [c] Not observed.

second with aryl groups σ-bonded to one silver atom and π-bonded to other silver atoms, a third in which both the first and the second types of bonding occur, and a fourth in which silver—silver bonds are also present. The Raman spectra rule out structures in which there is silver—silver bonding. The NMR spectra indicate the presence of only one type of aryl group, and therefore rule out the third possibility. From a comparison of the ^{13}C NMR spectral shifts of these silver compounds with those of well-known π-complexes of silver(I) salts [15] and of copper(I) salts [16], it is evident that π-interaction of the aromatic system with silver nuclei can also be ruled out. Thus, our data indicate that bridging aryl groups must be present in the arylsilver compounds I—V, as in the corresponding copper compounds.

The spectral data and the observed high molecular weight indicate that phenylsilver, like phenylcopper, is a coordination polymer containing phenyl groups bridging between two silver atoms (cf. ref. 11).

Whereas for the arylcopper compounds the introduction of one or more methyl groups in the phenyl ring causes the degree of association to drop to four, it was found that the same substitution in the case of the arylsilver compounds resulted in trimers throughout. Since coordinating ligands are absent, each silver atom will be linearly coordinated and thus the bridging carbon atoms are situated in the same plane as the three silver atoms. Consequently, we propose a symmetrical structure as shown in Fig. 1 for the trimeric species II—V. This is corroborated by the NMR spectra of the symmetrically-substituted compounds 4-methylphenylsilver (IV) and 2,6-dimethylphenylsilver (V) which are temperature independent within the range —95 to +10°C. The latter compound shows only one type of methyl group at all temperatures investigated. In a non-symmetrical structure, at least two different methyl peaks would be observed.

The NMR spectra of 2-methylphenylsilver (II) and of 3-methylphenylsilver (III) in which the aryl groups are asymmetrically substituted, show that in these cases configurational isomerism does occur. Whereas the ^{1}H and ^{13}C NMR spectra of 4-methylphenylsilver (IV) and 2,6-dimethylphenylsilver (V) are temperature independent, the spectra of 2-methylphenylsilver (II) and of 3-methylphenylsilver (III) change upon cooling. The ^{1}H NMR spectra of compound II (Fig. 2) reveal the existence of one type of methyl group at the coalescence temperature of —30°C and above. Below the coalescence temperature (<—35°C) the spectra show three different types of methyl groups.

The ^{13}C NMR spectra of compound II (Fig. 3) show rather broad absorptions for all carbon atoms at 0°C; at —35°C the resonance of C^6 is split up into three separate peaks, all other signals remaining rather broad. Since none of the spectra is concentration dependent, an intermolecular process is excluded, and the results must be accounted for by an intramolecular process. Both the ^{1}H and the ^{13}C NMR spectral data indicate that, as in the case of the corresponding copper compound, hindered rotation of the aryl groups around the C^1—C^4 axis results in the existence of several configurational isomers for compound II at low temperatures. At —30°C and above the aryl groups rotate fast enough to cause interconversion of the isomers, leading to an averaged spectrum. At —35°C and below, the rotation of the aryl groups is slowed down sufficiently

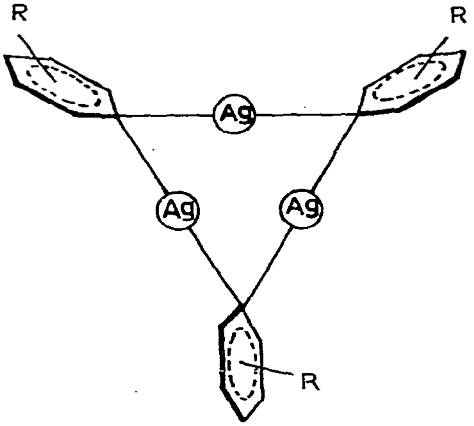


Fig. 1. Proposed structure for methyl-substituted arylsilver compounds.

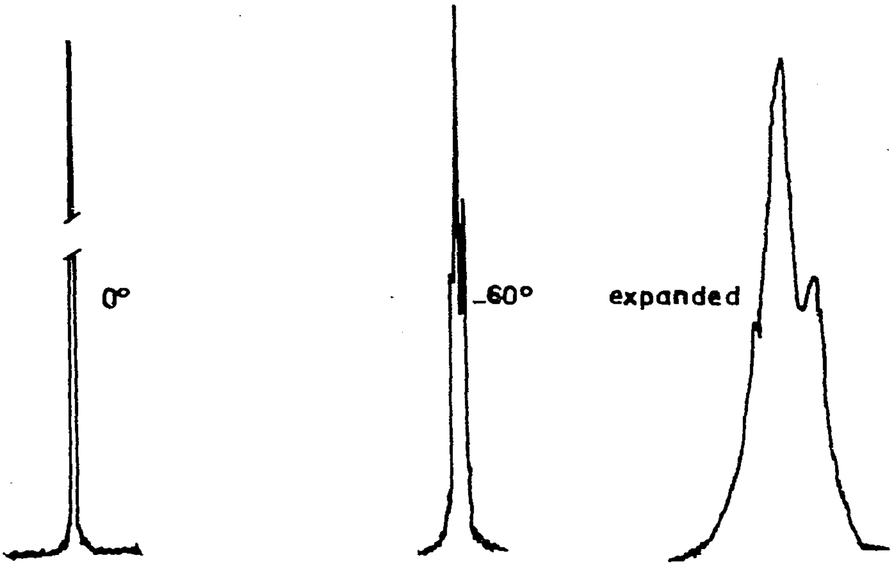


Fig. 2. ¹H NMR spectra (methyl-group region) of 2-methylphenylsilver (II).

to allow the observation of the two possible species in the NMR spectra. In our opinion the configurational isomers shown in Fig. 4 account for the observed spectra of 2-methylphenylsilver (II).

It appears that in these two isomers, three magnetically unequivalent kinds of methyl groups are present. Since the spectra show the presence of three methyl peaks it must be concluded that both configurational isomers are present below —30°C.

Temperature dependence was also observed in the NMR spectra of 3-methylphenylsilver (III). However, even at very low temperatures (—95°C) the signals were broad and so definite conclusions are not justified. The fact that even at these low temperatures no splitting of the methyl peak was observed can easily be understood by considering the rotational barrier for this compound. For steric reasons this barrier will be much lower for the *meta-* (III) than for the *ortho*-substituted compound (II) and therefore the coalescence temperature in the first case must be much lower.

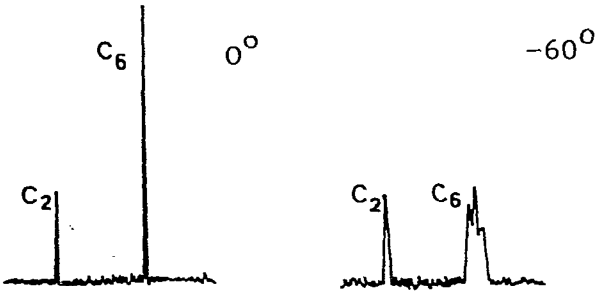


Fig. 3. ^{13}C NMR spectra (C^2 and C^6) of 2-methylphenylsilver (II).

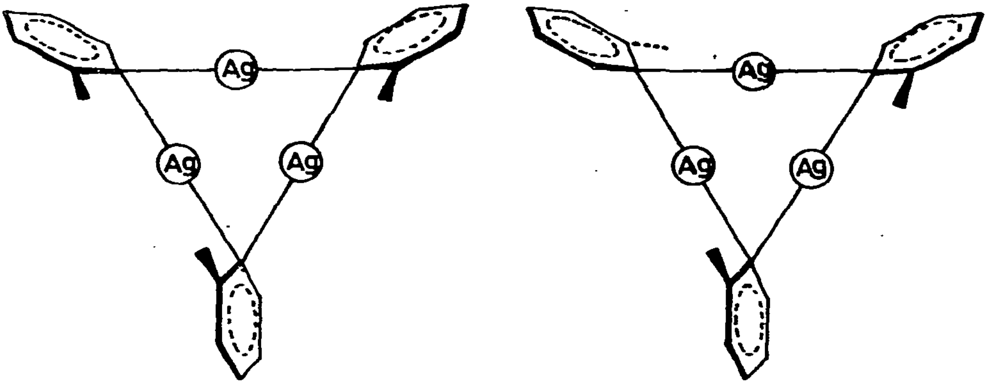


Fig. 4. Configurational isomers of 2-methylphenylsilver (II).

Experimental

General

All experiments were carried out under dry oxygen-free nitrogen. Solvents were carefully purified, and dried and distilled before use under nitrogen. Solvents, solutions and liquid reagents were handled by syringes.

IR spectra were recorded on a Perkin—Elmer 457 infrared spectrometer using Nujol mulls between KBr disks. Frequencies are accurate to ± 3 cm^{-1}.

NMR spectra were recorded on Varian EM-390 and XL-100/15 FT NMR spectrometers.

Decomposition temperatures were measured by differential thermal analysis and are accurate to ±2°C. Elemental analyses were carried out under the supervision of Mr. W.J. Buis, at the Analytical Department of the Institute for Organic Chemistry TNO, Utrecht.

The 3-methylphenylcopper and 4-methylphenylcopper, mentioned in this paper, were synthesized using the preparative method described in ref. 11.

Starting materials

The preparation and purification of the diarylzinc compounds used has been described in an earlier paper [11]. The silver nitrate was of AR grade and was used without further purification.

Synthesis of phenylsilver, 2-methylphenylsilver and 3-methylphenylsilver

Finely divided silver nitrate (5 mmol) was stirred with a solution of 10 mmol of diphenylzinc, bis(2-methylphenyl)zinc, or bis(3-methylphenyl)zinc, respectively, in 40 ml of diethyl ether. Initially, yellow to orange precipitates were formed. After 4—8 h stirring the precipitates had turned colourless. The compounds were washed with diethyl ether (5 × 25 ml) and pentane (2 × 25 ml) at —30°C. After drying in vacuo at 0°C the products were isolated in analytically pure form (overall yield 90—95%). Analytical date are presented in Table 4.

Synthesis of 4-methylphenylsilver and 2,6-dimethylphenylsilver

In these cases reactions in diethyl ether yielded products containing varying

TABLE 4

ANALYTICAL DATA OF ARYLSILVER COMPOUNDS

Compound	Analytical data (found (calcd.))		
	C	H	Ag
Phenylsilver	38.9 (38.96)	2.9 (2.72)	58.1 (58.32)
2-Methylphenylsilver	41.5 (42.25)	3.3 (3.53)	54.0 (54.22)
3-Methylphenylsilver	42.9 (42.25)	4.0 (3.53)	53.2 (54.22)
4-Methylphenylsilver	43.0 (42.25)	4.1 (3.53)	53.7 (54.22)
2,6-Dimethylphenylsilver	44.7 (45.07)	4.4 (4.23)	49.9 (50.66)

amounts of complexed silver nitrate. It appeared that pure products were formed when the reactions were carried out in THF solution at −30°C. Also here, initially yellow coloured products were formed, which decolourized very rapidly. After stirring for 10 h the products were washed with THF (5 × 25 ml) and pentane (2 × 25 ml). After drying in vacuo the products were obtained in analytically pure form. Analytical data are presented in Table 4.

Isolation of $C_6H_5Ag \cdot (AgNO_3)_2$

During the reaction of diphenylzinc with silver nitrate under the conditions mentioned above, initially an orange coloured product was formed. This product could be isolated in low yield by decantation. After washing with diethyl ether (5 × 25 ml) the product was dried in vacuo at 0°C. Anal.: Found: C, 13.7; H, 1.0; Ag, 61.6; N, 5.4; O, 18.3. $C_6H_6Ag_3N_2O_6$ calcd.: C, 13.73; H, 0.96; Ag, 61.67; N, 5.34; O, 18.29%.

Acknowledgements

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