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Synthesis and characterization of the lithium organoargentate salts $[Li(THF)_4][Ag(Triph)_2]\cdot THF$ and $[Li(THF)_4][Ag(C_6H_3\text{-}2,6\text{-}Mes_2)_2]\cdot 1/8OEt_2$ $(Triph = -C_6H_2\text{-}2,4,6\text{-}Ph_3;\ Mes = C_6H_2\text{-}2,4,6\text{-}Me_3)$

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Abstract

The synthesis and structural characterization of the new metal–terphenyl derivatives $[Li(THF)_4][Ag(Triph)_2]\cdot THF$ (**1**, Triph = C_6H_2-2,4,6-Ph_3) and $[Li(THF)_4][Ag(C_6H_3\text{-}2,6\text{-}Mes_2)_2]\cdot 1/8\ Et_2O$ (**2**, Mes = C_6H_2-2,4,6-Me_3) are described. Both compounds crystallize as solvent separated ion pairs that are composed of THF solvated Li^+ cations and argentate anions. The Li^+ cations are approximately tetrahedrally coordinated by four THFs in both structures. The silvers are essentially linearly coordinated by *ipso*-carbons of the aryl ligands with Ag–C distances in the range 2.048(15) to 2.112(10) Å with an average distance near 2.10 Å. These bond lengths clearly demonstrate that silver terphenyl complexes have a metal carbon distance that is ca. 0.2 Å longer than those in related copper complexes. Crystal data at 130 K with Cu–K_α ($\lambda = 1.54178$ Å) radiation: **1**, $a = 14.440(3)$, $b = 18.670(4)$, $c = 21.550(4)$ Å, $\beta = 104.25(3)°$, $Z = 4$, monoclinic, space group $P2_1/n$, $R_1 = 0.0741$ for 4589 ($I > 2(\sigma)I$) data, **2**, $a = 22.395(5)$, $b = 16.262(3)$, $c = 33.877(7)$ Å, $\beta = 104.79(3)°$, $Z = 8$, monoclinic, space group $P2_1/n$, $R_1 = 0.1288$ for 7553 ($I > 2(\sigma)$) data. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Argentate; Silver; Cyanate; Terphenyl

1. Introduction

Organometallic derivatives of silver(I) have received considerably less attention than their organocopper(I) counterparts [1]. This is probably a consequence of their less-widespread employment as synthetic reagents in comparison with the ubiquitous organocuprates. In addition, the greater cost of the silver derivatives has probably played a role in restricting their use. The terphenyl and related ligand derivatives of copper have proven to be a particularly interesting and unusual class of organocopper species. The controversial compound CuC_6H_2-2,4,6-Ph_3 and its silver analogue AgC_6H_2-2,4,6-Ph_3 [2] were said to possess the first examples of one-coordinate metals in the solid state. Subsequent reinterpretation of their structural and spectroscopic data cast considerable doubt on their formulation, however [3]. In addition, experimental work on related solvated, e.g. 2,4,6-$Ph_3H_2C_6Cu(\mu\text{-}C_6H_2\text{-}2,4,6\text{-}Ph_3)$-$Cu(SMe_2)_2$, [4] and unsolvated, e.g. $(CuC_6H_3\text{-}2,6\text{-}Ph_2)_3$, [5] copper species bearing identical or almost identically sized substituents indicated that association of the putative monomers could indeed occur to give species with previously unobserved structures. Another unusual feature of the original report on the MC_6H_2-2,4,6-Ph_3 (M = Cu or Ag) species was that the reported M–C distances were almost identical, in spite of the fact that the effective ionic radius of two-coordinate Ag^+ is ca. 0.2 Å larger than two-coordinate Cu^+ [6]. The structures of terphenyl complexes of silver are therefore of significance in establishing whether or not there are any unique features associated with the M–C distances in these derivatives. In this paper the structures of two new organo silver(I) derivatives of terphenyl ligands are reported. Their Ag–C distances, which average ca. 2.10 Å in length, are ca. 0.2 Å longer than those in related copper complexes.

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2. Experimental

2.1. General procedures

All experiments were performed under a nitrogen atmosphere either by using modified Schlenk techniques or in a Vacuum Atmospheres HE43-2 drybox. Solvents were freshly distilled from a sodium–potassium alloy and degassed twice prior to use. The ^{13}C-, ^{1}H- and ^{7}Li-NMR spectra were recorded in C_6D_6 or THF-D_8 solutions by using a General Electric QE-300 NMR spectrometer. The compounds $(Et_2O)_2$LiTriph [7] and $(LiC_6H_3\text{-}2,6\text{-}Mes_2)_2$ [8] were synthesized by literature procedures. Silver cyanate was obtained commercially and used as received.

2.2. $[Li(THF)_4][Ag(Triph_2)]\cdot THF$

$(Et_2O)_2$LiTriph (2.30 g, 5.0 mmol) was dissolved in Et_2O (30 ml) and the solution was added dropwise to a rapidly stirred suspension of AgOCN (0.37 g, 2.50 mmol) in a 3:1 Et_2O–THF mixture (20 ml) and cooled to ca. −78°C. During the reaction, light was excluded by wrapping the Schlenk tube with aluminum foil. After 2 h stirring at ca. −78°C, the mixture was allowed to warm to ca. 0°C over 3 h. The gray precipitate was then removed by filtration. The resultant pale-green filtrate was stored in a ca. −20°C freezer for 3 days to afford the product as colorless crystals: yield 0.94 g (35%); m.p.: 122–124°C dec. ^{1}H-NMR (C_6D_6, 25°C) δ 7.79, (br, s); 7.72 (d, $J = 6.0$ Hz); 7.65 (d, $J = 6.0$ Hz); 7.56 (br, s); 7.32 (d, $J = 6.0$ Hz); 7.17 ∼ 6.96 (m) [aromatic H's]; 7.15 (C_6D_6); 2.99 (br, s, THF); 0.93 (br, s, THF). ^{13}C{^{1}H}-NMR (C_6D_6, 25°C) δ 192.23 (*i*-C_6H_2); 153.76 (*o*-C_6H_2); 153.04 (*p*-C_6H_2); 144.59 (*i*-(*o*-Ph)); 143.76 (*i*-(*p*-Ph)); 142.85 (*o*-(*p*-Ph)); 141.52 (*p*-(p-Ph)); 137.68 (*m*-(p-Ph)); 129.10 (*m*-C_6H_2); 128.00 (t, C_6D_6); 125.52 (*p*-(*o*-Ph)); 125.04 (*o*-(*o*-Ph)); 121.89 (*m*-(*o*-Ph)); 68.18 (THF); 25.24 (THF). ^{7}Li-NMR (C_6D_6, 25°C: LiCl in D_2O was used as a reference) δ 1.49 ppm (br, s).

2.3. $[Li(THF)_4][Ag(C_6H_3\text{-}2,6\text{-}Mes_2)_2]\cdot 1/8\ Et_2O$

$(LiC_6H_3\text{-}2,6\text{-}Mes_2)_2$ (1.6 g, 5.0 mmol) was dissolved in Et_2O (30 ml) and added dropwise to a stirred suspension of AgOCN (0.37 g, 2.50 mmol) in a 3:1 Et_2O–THF mixture (20 ml) and cooled to ca. −78°C. Light was excluded by wrapping the Schlenk with aluminum foil during the reaction. After 2 h stirring at ca. −78°C, the mixture was allowed to warm to ca. 0°C, whereupon the gray residue was filtered off. The yellow–green supernatant liquid was placed in a −20°C freezer for 1 day, which afforded the product **2** as colorless crystals: yield: 1.97 g (37.9%); m.p.: the white crystalline became light-brown at 134°C and decomposed to a black powder at 150–152°C. ^{1}H-NMR (THF-d_8, 25°C) δ 6.59 (t, $J = 7.2$ Hz, *p*-C_6H_3); 6.54 (s, *m*-Mes); 6.32 (d, $J = 7.2$ Hz, *m*-C_6H_3); 3.58 (br, THF-d_8); 2.13 (br, s, *o*-CH_3 (Mes)); 1.74 (br, THF-d_8); 1.59 (br, s, *p*-CH_3(Mes)). Small peaks at 3.34 (q) and 1.08 (t) ppm were assigned to Et_2O (solvant) which, upon integration, afforded an intensity ratio of 0.13:1 with respect to the cation and anion peaks. ^{13}C{^{1}H}-NMR (THF-d_8, 25°C) δ 180.89 (br, *i*-C_6H_3); 152.09 (*i*-Mes); 148.93 (*o*-C_6H_3); 136.36 (*o*-Mes); 132.27 (*p*-Mes); 128.75 (*p*-C_6H_3); 127.50 (*m*-Mes); 121.91 (*m*-C_6H_3); 67.41 (quintet, THF-d_8); 25.32 (quintet, THF-D_8); 21.89 (*o*-$C$$H_3$(Mes)); 21.51 (*p*-$C$$H_3$(Mes)) very small peaks at 59.21 and 15.65 ppm were assigned to be Et_2O (solvent). ^{7}Li-NMR (THF-d_8, 25°C: LiCl–D_2O was used as reference) δ −0.62 ppm (br, s).

2.4. X-ray data collection, the solution and refinement of the structures

The crystals were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. Suitable crystals were selected, attached to a glass fiber, and immediately placed in the low-temperature N_2 stream [9]. Both X-ray data sets were collected with Cu–K_α ($\lambda = 1.54178$ Å) radiation by using a Siemens P4RA diffractometer equipped with a rotating anode X-ray source, nickel filter and a locally modified LT apparatus. Calculations were carried out on a Micro Vax 3200 computer using the SHELXTL-PLUS [10] program system. The structures were solved by direct methods. The data were subsequently refined by full-matrix least-squares procedures. Hydrogen atoms were included by the use of a riding model with C–H distance of 0.96 Å and fixed isotropic thermal parameters with $U_H(\text{iso}) = 0.06$ Å^2. For the absorption correction, an empirical method, XABS2, was applied [11]. Although the data for **1** generally refined satisfactorily, there were residual electron density values of 1.79 and 1.44 e Å^{-3} that were 1.226 and 1.339 Å distant from the silver. These probably resulted from absorption problems associated with use of copper radiation. For **2**, the higher than usual R value is probably due to disorder problems in the $Li(THF)_4$ and OEt_2 (solvent) groups. The atoms in these groups were located from successive difference maps. But poor convergence during refinement was observed, probably as a result of their large thermal motion. For several of these atoms, more reasonable geometries were obtained from the difference map positions than from those obtained after anisotropic refinement. Consequently, the original positions were retained and their isotropic thermal parameters were simply fixed at a relatively high value of 0.15 Å^2 by use of the SHELXTL AFIX1 feature during the final cycle of the refinement. Both Li(2) and C(117) were successfully modeled with two split positions; Li(2A) and Li(2B) (50:50) and C(117)

Table 1
Selected data collection parameters for **1** and **2** [a]

Compound	$[Li(THF)_4]$-$[Ag(Triph_2)]$ ·THF	$[Li(THF)_4]$-$[Ag(C_6H_3\text{-}2,6\text{-}Mes)_2]\cdot 1/8$ OEt_2
	$C_{68}H_{74}AgLiO_5$	$C_{64.50}H_{83.25}AgLiO_{4.13}$
Formula weight	1086.08	1039.37
Crystal color/habit	Colorless/block	Colorless/block
Crystal size (mm)	0.36 × 0.10 × 0.04	0.22 × 0.20 × 0.14
Unit cell dimensions		
a (Å)	14.440(3)	22.395(5)
b (Å)	18.670(4)	16.262(3)
c (Å)	21.550(4)	33.877(7)
β (°)	104.25(3)	104.79(3)
V (Å^3)	5631.0(19)	11929(4)
Z	4	8
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
$D_{calc.}$ (g cm^{-3})	1.281	1.257
Absorption coefficient (mm^{-1})	3.260	3.039
Trans. coefficient	0.88–0.39	0.68–0.55
2θ range (°)	0–113	0–113
Number of unique data	14 855	15 452
Observed reflections ($I > 2\ \sigma(I)$)	4589	7553
R^2, wR^2	0.0741, 0.1549	0.1288, 0.3116

[a] $R^1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR^2 = \Sigma||F_o| - |F_c||$, $w^{1/2}/\Sigma|F_o|$, $w^{-1} = \sigma^2(F_o^2) + (0.0663P)^2 + 4.49P$ $(P = (F_o^2 + 2F_c^2)/3)$. Data were collected at 130 K using Cu–K$_\alpha$ radiation ($\lambda = 1.54178$ Å), Siemens P4RA.

and C11A (50:50), respectively. Finally, the solvent (diethyl ether) molecules were most suitably refined with quarter occupancy. The crystal data for this compound was also recollected with Siemens R3 m/V diffractometer with Mo–K$_\alpha$ ($\lambda = 0.71069$ Å) radiation. However, no improvement in the data was obtained. An abbreviated list of data collection parameters and some important structural details are provided in Tables 1 and 2, respectively.

3. Discussion

The compounds **1** and **2** were synthesized by the reaction of the respective lithium reagents with silver cyanate, AgOCN. This reagent was chosen for its greater solubility than the silver halides. In addition it had already been shown that AgOCN was a suitable precursor for the synthesis of silver amides $(AgNR_2)_4$ [12]. Attempts to use silver chloride in the synthesis of **1** and **2** eventually led to decomposition and the isolation of the respective arenes and a gray solid which contained elemental silver.

The ion-pair argentate structures of **1** and **2** were suggested by ^{1}H, ^{13}C and ^{7}Li solution NMR spectroscopy. The ^{13}C{^{1}H}-NMR spectra each revealed a peak at low field (i.e. at δ 192.23 (**1**) and 180.89 (**2**)) attributable to the *ipso*-C atom of the central aromatic ring. These shifts are comparable to those previously described for cuprates [13].

The ionic structures of **1** and **2** were confirmed by single-crystal X-ray diffraction studies. Both structures were marred by disordering coupled with relatively high thermal motion, both in the cation and in the solvent molecules of crystallization. Such disorder is a common feature of this general structure type. There were also minor absorption problems owing to the use of copper radiation in conjunction with crystals containing silver atoms. Nonetheless, these problems do not affect the overall interpretation of the structure in any significant way.

The structures of **1** (Fig. 1) and **2** (Fig. 2) consist of well-separated cations and anions. In **1** the THF molecule of crystallization (see Fig. 1) shows no interaction with either the Li$^+$ or Ag$^+$ ions. The Li$^+$, which is bound to four THF donors, has distorted tetrahedral coordination with O–Li–O angles in the range 103.6(7) to 114.9(7)°. The Li–O distances, which average 1.92(1)

Table 2
Some important bond distances (Å) and bond angles (°) for **1** and **2**

	$[Li(THF)_4][Ag(Triph_2)]\cdot$THF **(1)**		$[Li(THF)_4][Ag(C_6H_3\text{-}2,6\text{-}Mes)_2]\cdot 1/8\ OEt_2$ **(2)**	
Ag–C(ipso)	Ag(1)–C(1) 2.091(9) (avg = 2.097(9))	Ag(1)–C(25) 2.103(9)	Ag(1)–C(1) 2.107(18) Ag(2)–C(49) 2.048(15) (avg = 2.09(3))	Ag(1)–C(25) 2.112(19) Ag(2)–C(73) 2.098(13)
Li–O (avg)	1.921(6)		1.92(18)	
C–Ag–C	C(1)–Ag(1)–C(25) 176.7(4)		C(1)–Ag(1)–C(25) 177.4(6)	C(49)–Ag(2)–C(73) 176.0(7)

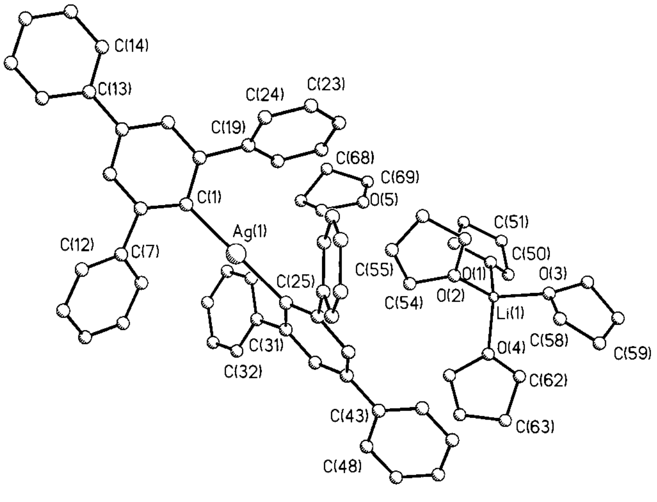

Fig. 1. Computer-generated drawing of **1**. H atoms are not shown for clarity.

Å, are similar to those previously observed for this type of cation [14]. The $[Ag(Triph)_2]^-$ and $[Ag(C_6H_3\text{-}2,6\text{-}Mes_2)_2]^-$ anions consist of silver bound to two aryl groups through their *ipso*-carbon atoms. The silver coordinations are almost linear with C–Ag–C angles of 176.7(4) and 176.8(8)°. The Ag–C distances, which average 2.097(9) and 2.09(3) Å, are shorter than the 2.162(7) and 2.198(7) Å in $[Li(THF)_4][Ag\{C(SiMe_3)_3\}_2]$ [15] or the average Ag–C distances seen in the anions $[Li_2Ag_3Ph_6]^-$ [16] (2.13 Å) and $[Ag\{\overline{CS(O)_2(CH_2)_3S}(O)_2\}_2]$ [17] (2.14 Å). However, they are comparable to the two Ag–C bond lengths (2.191(7) and 2.015(35) Å) reported for $[Ag\{CF(CF_3)_2\}_2]^-$ [18]. It appears, therefore, that the Ag–C bond lengths 2.091(9) and 2.103(9)Å in **1** are at the low end of the currently known range of Ag–C distances in diorgano argentates [1,15–18]. The difference in size between the Triph and $-C_6H_3\text{-}2,6\text{-}Mes_2$ substituents in the structures of **1** and **2** is reflected in the fact that the torsion angles between the aryl rings attached to silver is 56.5° for **1** and has an average value of 83.4° for **2**.

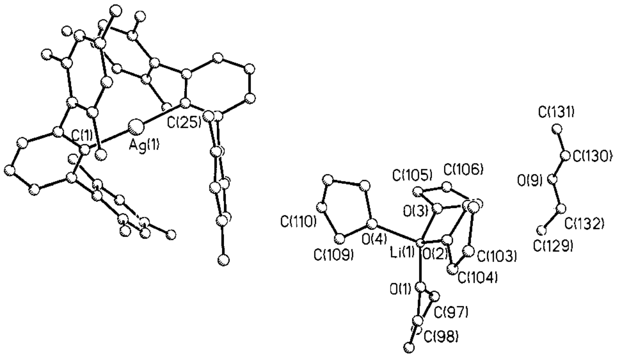

Fig. 2. Computer-generated drawing of **2**. Molecule 2 in the asymmetric unit is omitted and H atoms are not shown for clarity.

The structures of **1** and **2** may also be compared with related organocuprate species, for instance the compound $LiCu\{C_6H_3\text{-}2,6\text{-}Ph_2\}_2$ [5] which has a contact ion-pair structure composed of a $[Cu\{C_6H_3\text{-}2,6\text{-}Ph_2\}_2]^-$ and a Li^+ cation. The latter associates with the anion through an η^6–π interaction with one of the *ortho*-Ph substituents. The Cu–C distances in the anion are 1.922(5) and 1.957(5) Å, which are slightly longer than the values seen in the related copper terphenyls; 1.906(4) Å in $[Li(THF)_2\{Cu(CN)C_6H_3\text{-}2,6\text{-}Trip_2\}_2]_2$ [19] (Trip = $-C_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3$) or 1.894(6) Å in the neutral monomer $(Me_2S)CuC_6H_3\text{-}2,6\text{-}Trip_2$ [20]. The consistency and relatively narrow range of the Cu–C distances in this group of compounds show that Cu–C distances in terphenyl and related copper compounds are roughly 0.2 Å shorter than those in the corresponding silver species reported here. This is, of course, in harmony with the different covalent and ionic radii of copper and silver which differ by a similar amount. The structure of **2**, although not as accurate as that of **1**, validates the important structural parameters at silver; i.e. almost linear coordination of the Ag^+ ion and very similar Ag–C distances.

In summary, the data for the argentate ions in **1** and **2** are in agreement with each other and confirm that the Ag–C bonds in these terphenyl derivatives are 0.2 Å longer than the Cu–C bonds in closely related copper species. Thus, these results do not support the almost equal Cu–C = 1.890(6) Å and Ag–C = 1.902(5) Å distances reported for $MC_6H_2\text{-}2,4,6\text{-}Ph_3$ [2] and lend further support to the reassessment of Haaland and co-workers, which suggested that each of these compounds mostly consisted of the starting material $BrC_6H_2\text{-}2,4,6\text{-}Ph_3$ [3].

4. Supplementary material

The X-ray data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-121767 and CCDC-121768. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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