Journal of Organometallic Chemistry, 55 (1973) 419–425
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BIS{2-[(DIMETHYLAMINO)METHYL]PHENYL}SILVERLITHIUM, A TETRANUCLEAR ORGANOMETALLIC COMPOUND WITH BRIDGING ARYL GROUPS BETWEEN SILVER AND LITHIUM

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(Received October 31st, 1972)

SUMMARY

Bis{2-[(dimethylamino)methyl]phenyl}silverlithium has been prepared and characterized. Molecular weight determinations, and ^{13}C NMR and ^{1}H NMR spectra reveal that the compound exists (in benzene) as a tetranuclear mixed metal cluster containing aryl groups bridging the silver and lithium atoms. Silver–proton, silver–carbon and lithium–carbon couplings have been observed in the NMR spectra of this compound.

INTRODUCTION

Up to now only a few organoargentates $(R_2Ag)_n^{n-}M^{n+}$ have been described in the literature*, *viz* dialkynylsilverpotassium and -barium compounds[2] and bis(pentafluorophenyl)silverlithium[3]. The structure of the latter is unknown, while the complex acetylides are assumed to contain linear dialkynylsilver anions, $(R{-}C{\equiv}C{-}Ag{-}C{\equiv}C{-}R)^-$. Such anions are also present (in the solid state) in the trimethylphosphine complex of (phenylethynyl)silver[4], *viz* $[R_2Ag^- \cdot (R'_3P)_2Ag^+]_n$.

In connection with our work on stable σ-bonded organocopper[5–8] and organosilver compounds[8,9] we have studied some "ate" complexes of these metals. In a recent communication[10] from this laboratory the preparation and characterization of bis{2-[(dimethylamino)methyl]phenyl}copperlithium were described. In the present paper we report on the corresponding silverlithium compound.

RESULTS AND DISCUSSION

In a preliminary experiment, {2-[(dimethylamino)methyl]phenyl}silver[8,9] was added to a suspension of an equivalent amount of the corresponding organolithium compound in benzene. The ^{1}H NMR spectrum of the resulting clear solution revealed that both the organolithium and the organosilver compound had disappeared from the solution. Obviously a new compound had formed which was supposed to be the argentate [eqn. (1)]. The same compound was obtained by

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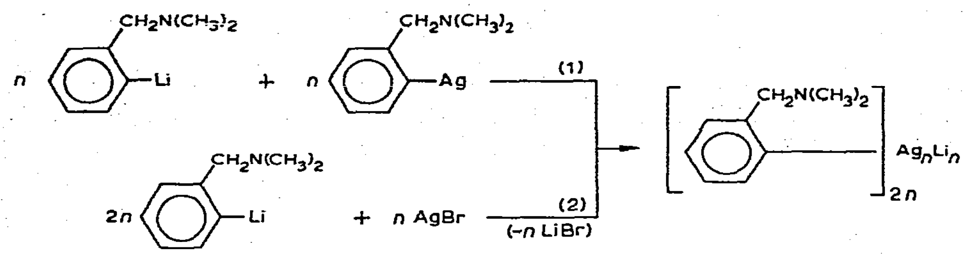
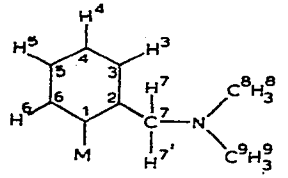
* For a review see ref. 1.



treating the organolithium compound with silver bromide (2/1 ratio) in diethyl ether [eqn. (2)]. From this reaction a cream coloured solid was isolated, which decomposed at about 180° and was sensitive towards oxygen and water. Molecular weight determinations in benzene (by cryoscopy and ebullioscopy) indicated that the compound exists as a dimer ($n=2$) in this solvent. The structure of the $R_4Ag_2Li_2$ molecule follows from the ^1H and ^{13}C NMR spectra.



In the ^1H NMR spectrum (60 and 100 MHz, room temperature, solvent C_6D_6, internal standard TMS) the CH_3 (H_8 and H_9) protons appear as a singlet at 1.74 ppm, the CH_2 (H_7 and $H_{7'}$) protons as two doublets [J(H–H) 12.0 Hz] at 2.52 and 3.96 ppm downfield from TMS. The aromatic part of the ^1H NMR spectrum (100 MHz) is shown in Fig. 1b. The H_6 proton appears as a triplet of doublets at 8.67 ppm; the triplet splitting (~7 Hz both in the 60 MHz and 100 MHz spectra) obviously arises from two *ortho*-interactions of almost the same magnitude, *viz.* coupling of H_6 with H_5 and with M. The absolute value of the H–C–C–M coupling as well as the observed pattern* for H_6 indicate that coupling occurs with silver**. The occurrence of metal–proton coupling could also be demonstrated by proton spin-decoupling experiments. Irradiation at H_3 and H_4 does not change the pattern of H_6 considerably; irradiation at H_5 results in a doublet (silver–proton coupling) for H_6 (see Fig. 1a). The patterns of the signals due to the other aromatic protons suggest that these protons also couple with the silver atom. For example, the signal due to H_5 appears as a triplet as a result of two *ortho*-interactions (with H_4 and H_6) and two *meta*-interactions (with H_3 and silver) of almost the same magnitude. Without metal–proton coupling the signals due to H_6 and H_5 would be expected to appear as a doublet of doublets (H_6, one *ortho*- and one *meta*-coupling) and as a triplet of doublets (H_5, two *ortho*- and one *meta*-coupling). In fact this has been observed in the spectrum of the corresponding cuprate[10] (coupling with copper is not observed probably because of quadrupole relaxation) and in the simulated spectrum without silver–proton couplings. In Fig. 1c

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* Coupling of H_6 with H_5 and with ^7Li ($I=\frac{3}{2}$) would result in an 8-line pattern; a very weak H–C–C–Li coupling (< 0.5 Hz) can not be excluded.

** Natural abundance ^{107}Ag ($I=\frac{1}{2}$) 51.8%, ^{109}Ag ($I=\frac{1}{2}$) 48.2%.

the calculated spectrum (superimposed spectra for ^{107}Ag and ^{109}Ag) in the aromatic region has been presented; the data used in the simulation have been collected in Table 1. The agreement of the observed spectrum (Fig. 1b) with the simulated one (Fig. 1c)

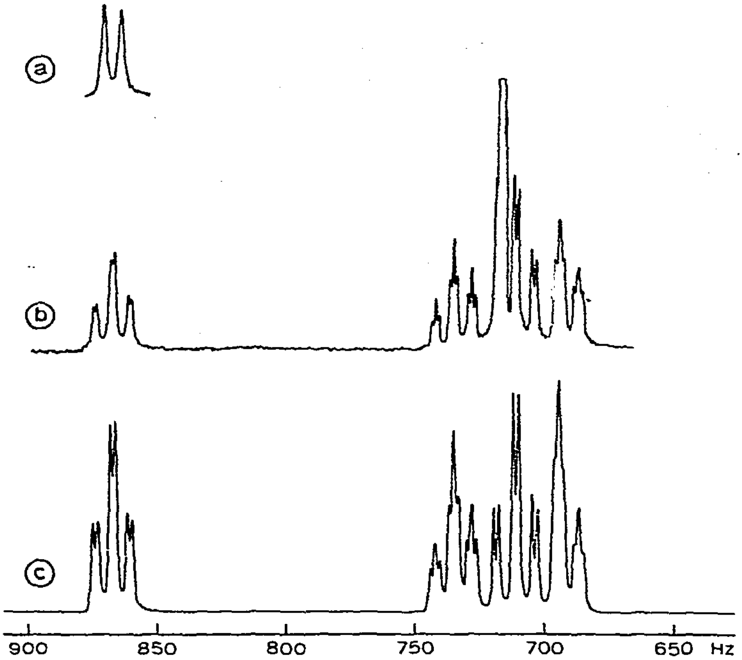

Fig. 1. The aromatic region (H_3–H_6) of the ^1H NMR spectrum at 100 MHz. (a) The H_6 signal with irradiation at H_5. (b). The observed spectrum. (c) The simulated spectrum (line width 1.00 Hz, see also Table 1).

TABLE 1

CHEMICAL SHIFTS AND COUPLING CONSTANTS USED IN THE CALCULATION OF THE ^1H NMR SPECTRUM AT 100 MHz

Chemical shifts (Hz)					
H_3	691.0	H_5	734.0	H_7	396.0
H_4	710.5	H_6	866.5	$H_{7'}$	252.0
Coupling constants (Hz)					
H_3–^{107}Ag	−1.6	H_3–H_4	7.8	H_6–H_7	0.2
H_3–^{109}Ag	−1.8	H_3–H_5	2.0	H_6–$H_{7'}$	0.3
H_4–^{107}Ag	0.3	H_3–H_6	0.4	H_7–$H_{7'}$	−12.0
H_4–^{109}Ag	0.3	H_3–H_7	−0.5		
H_5–^{107}Ag	−1.5	H_3–$H_{7'}$	−0.6		
H_5–^{109}Ag	−1.7	H_4–H_5	7.3		
H_6–^{107}Ag	−6.2	H_4–H_6	1.9		
H_6–^{109}Ag	−7.1	H_4–H_7	0.2		
H_7–^{107}Ag	0.4	H_4–$H_{7'}$	0.3		
H_7–^{109}Ag	0.4	H_5–H_6	7.0		
$H_{7'}$–^{107}Ag	0.5	H_5–H_7	−0.3		
$H_{7'}$–^{109}Ag	0.5	H_5–$H_{7'}$	−0.4		

reveals that the absolute values of the coupling constants used in the simulation are almost correct. One doublet of the H_4 signal is masked by the signal due to C_6HD_5 present in the solvent; however, this doublet has been observed using deuterated toluene as a solvent as well as in the 60 MHz spectrum.

From the above it must be concluded that only *one type of aryl group is present*, and that *this aryl group is bound to one silver atom.*

In the ^{13}C spectrum the signals due to C_2–C_9 were found in the expected regions: C_7, C_8 and C_9 (one singlet) upfield from benzene, C_3–C_5 in the benzenic region and C_2 and C_6 downfield from benzene. The signals due to C_2, C_3, C_5–C_7 in fact are doublets which has been ascribed to coupling with silver*. The most interesting part of the spectrum is the complex pattern at the lowest field (at about 170 ppm downfield from TMS) which obviously arises from the C_1 carbon bound directly to the metal. This part of the ^{13}C spectrum is shown in Fig. 2b. As can be seen from Fig. 2a the multiplicity of this signal can be accounted for by assuming a *coupling of* C_1 *with one silver atom* [$J(^{13}C\text{–}^{107}Ag) = 118.3 \pm 0.8$ Hz, $J(^{13}C\text{–}^{109}Ag) = 136.0 \pm 0.8$ Hz] and *with one lithium atom* [$J(^{13}C\text{–}^{7}Li) = 7.2 \pm 0.2$ Hz]. The combined ^{1}H and ^{13}C NMR data in the aromatic region point out that all four aryl groups in $R_4Ag_2Li_2$ are bound in the same manner, *i.e. each aryl group bridges one silver and one lithium atom.*

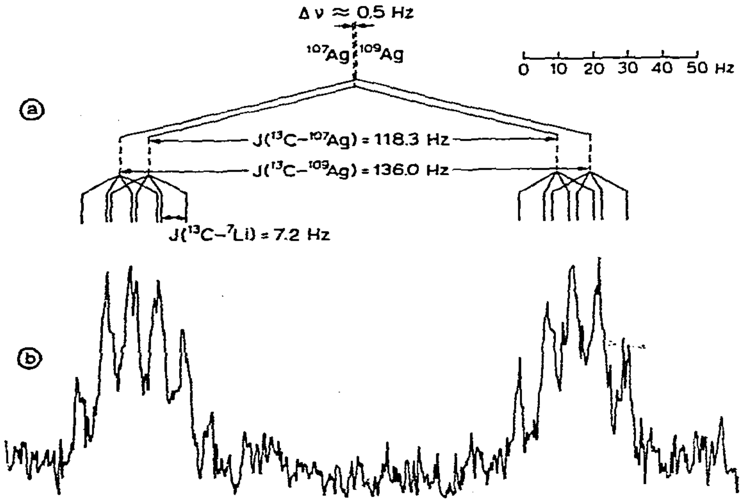

Fig. 2. The low field region (C_1) of the ^{13}C NMR spectrum at 25.2 MHz. (a) The expected spectrum with large C–Ag and small Li–C coupling constants. (b) The observed spectrum.

The NCH_3 and NCH_2 proton resonance patterns at room temperature indicate that the $-CH_2N(CH_3)_2$ ligands are coordinated to the same metal atom. In view of the HSAB principle we assume that these nitrogen ligands are bound to the

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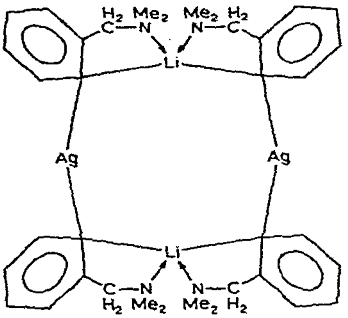
* A detailed account of the ^{13}C NMR spectrum of related arylsilver compounds will be published in the near future[19].

lithium atom. Thus the following structure is indicated*:



As mentioned above the CH_2 protons H_7 and $H_{7'}$ appear as two doublets (*geminal* coupling of 12 Hz) at 3.96 and 2.52 ppm, while the CH_3 protons H_8 and H_9 appear as a singlet at 1.74 ppm. Upon heating (in toluene-d_8) the signals due to H_7 and $H_{7'}$ collapse at about 90° (singlet at 3.30 ppm). Upon cooling the signals due to H_8 and H_9 appear as two singlets at 1.33 and 2.03 ppm (at $-10°$); these signals collapse at about $+10°$. These changes in the proton signal pattern with the temperature can be explained by a rapid exchange at higher temperatures between N(coordinated) and N(free).

A similar study of the "ate" complex derived from (2,4,6-trimethoxyphenyl)-silver[8,9] was less succesful. In the ^{13}C NMR spectrum of a 1/1 mixture of (2,4,6-trimethoxyphenyl)silver and (2,4,6-trimethoxyphenyl)lithium no resonances due to the carbon bound to the metal atom could be detected. The ^1H NMR spectra of mixtures of the organosilver and -lithium compounds (ratio RLi/RAg 20/80 up to 60/40) indicated that the original species RAg and RLi are not present as such in the solution (solvent deuterated benzene), since only one *ortho*-methoxy and one *para*-methoxy signal was observed. Even a very fast exchange between RAg and RLi, or between R_2AgLi and RAg (if excess RAg is present) must be excluded from the chemical shifts of the *ortho*- and the *para*-methoxy protons of the various mixtures. Most probably various species $R_mAg_{m-n}Li_n$ ($m > 2$) are present in solution; at room temperature rapid exchange phenomena between these species occur.

CONCLUSIONS

This study reveals that this particular "argentate" consists of a tetranuclear silver-lithium cluster with aryl groups bridging the silver and lithium atoms. This appears to be the first demonstration of bridging phenyl groups in an organosilver compound. The occurrence of bridging phenyl groups has recently been proved for the corresponding organocopperlithium[10] and organocopper compounds[11,12,]**.

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* In the proposed structure lithium–lithium and lithium–silver bonding is less probable; silver–silver bonding cannot be excluded.

** The only other compounds in which the presence of bridging phenyl groups has been demonstrated so far are: Ph_6Al_2[15], $Ph_2Me_4Al_2$[16] and trinuclear osmium complexes[17,18], *e.g.* $Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$.

The great similarity between the organic compounds of the first two elements of Group Ib suggests that the phenomenon of bridging organic groups in organosilver compounds may be quite general.

Furthermore, the occurrence of silver–proton and silver–carbon coupling has been demonstrated for the first time. (Silver–fluorine coupling has been observed before[13,14]).

EXPERIMENTAL

General

All reactions were carried out in an atmosphere of dry oxygen-free nitrogen. Solvents were carefully purified, dried and distilled before use in an atmosphere of nitrogen.

The NMR spectra were recorded using Varian Associates T-60 (^1H), HA-100 (^1H) and XL-100/15 FT (^{13}C) NMR spectrometers. The ^1H spectrum was analyzed as an XABCDEF spectrum in an interactive iterative procedure with the spin simulation program SIMEQ of Kort and Van der Haak* on a Varian Spectrosystem 100.

Bis{2-[(dimethylamino)methyl}silverlithium

A mixture of equimolar amounts (60 mmoles) of butyllithium and *N,N*-dimethylbenzylamine in 230 ml of diethyl ether was left at room temperature for about 90 h. This solution was cooled to −50° and silver bromide (30 mmoles) was added. The resulting mixture was stirred for 1 h at −50° and subsequently allowed to attain room temperature. The solvent was removed from the greyish-coloured solid by decantation. Ether (20 ml) was added and again decanted. The resulting solid was dried *in vacuo* and treated with 3 × 50 ml of benzene giving a black-brown residue A and dark but clear extracts (separated by centrifugation). The benzene was removed from the combined extracts *in vacuo* leaving a light-brown-coloured solid. This solid was dissolved in 35 ml of benzene (at 35° complete dissolution); the solution was cooled to 10° and 35 ml of n-pentane was added. A cream-coloured solid precipitated. The pentane/benzene mixture was decanted; a part of the solvent (mainly pentane) was condensed on the solid by low temperature distillation and subsequently the liquid was decanted. This procedure was repeated three times. The remaining cream-coloured solid consisted (after drying *in vacuo*) of pure bis{2-[(dimethylamino)methyl]phenyl}silverlithium as appears from the ^1H NMR spectrum. [Yield about 2 g, decompn. temp. 180°. $(C_{18}H_{24}AgLiN_2)_n$ calcd.: mol. wt. 383.2 *n*. Found: mol. wt. cryoscopic in benzene, 765, 777, 905 ($\bar{n}$ 2.1); mol. wt. ebullioscopic in benzene, 703, 742 ($\bar{n}$ 1.9).] A second treatment of solid A afforded about 2 g of the argentate contaminated with some of the organosilver compound $[(RAg)_n]$.

ACKNOWLEDGEMENTS

The authors are much indebted to Dr. M. J. A. de Bie and Mr. J. P. C. M. van Dongen (Laboratory of Organic Chemistry, State University of Utrecht) for recording the ^{13}C spectra and for helpful discussions, and to Miss T. G. Meerbeek for able experimental assistance.

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REFERENCES

1 C. D. M. Beverwijk, G. J. M. van der Kerk, A. J. Leusink and J. G. Noltes, *Organometal. Chem. Rev. A*, 5 (1970) 215.
2 R. Nast and H. Schindel, *Z. Anorg. Allg. Chem.*, 326 (1963) 201.
3 V. B. Smith and A. G. Massey, *J. Organometal. Chem.*, 23 (1970) C9.
4 P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, 20 (1966) 502.
5 G. van Koten, A. J. Leusink and J. G. Noltes, *J. Chem. Soc. D*, (1970) 1107.
6 G. van Koten, A. J. Leusink and J. G. Noltes, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 227.
7 G. van Koten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, (1972) 59.
8 G. van Koten, A. J. Leusink and J. G. Noltes, *Abstr. Pap. Vth Int. Conf. Organometal. Chem.*, Moscow 1971, Vol. 1, p. 484.
9 A. J. Leusink, G. van Koten and J. G. Noltes, to be published.
10 G. van Koten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, (1972) 446.
11 J. M. Guss, R. Mason, I. Sotofte, G. van Koten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, (1972) 446.
12 J. M. Guss, R. Mason, R. M. Thomas, G. van Koten and J. G. Noltes, *J. Organometal. Chem.*, 40 (1972) C79.
13 V. R. Polishchuk, L. A. Fedorov, P. O. Okulevich, L. S. German and I. L. Knunyants, *Tetrahedron Lett.*, (1970) 3933.
14 W. T. Miller, R. H. Snider and R. J. Hummel, *J. Amer. Chem. Soc.*, 91 (1969) 6532.
15 J. F. Malone and N. S. McDonald, *Chem. Commun.*, (1967) 444.
16 J. F. Malone and N. S. McDonald, *J. Chem. Soc. D*, (1970) 280.
17 C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland and R. Mason, *J. Chem. Soc., Chem. Commun.*, (1972) 87.
18 G. J. Gainsford, J. M. Guss, P. R. Ireland, R. Mason, C. W. Bradford and R. S. Nyholm, *J. Organometal. Chem.*, 40 (1972) C70.
19 C. D. M. Beverwijk, J. P. C. M. van Dongen and G. J. M. van der Kerk, to be published.