fractions proved (by TLC) to be mixtures. Later **6** eluted: 0.758 g (51%); mp 107–110 °C.

An analytical sample, mp 109–110 °C, was obtained by recrystallization from a mixture of toluene and 60–80 °C petroleum ether: IR (KBr) 3390, 1590, 1470, 1360, 1310, 1250, 1070, 740, 690 cm^{-1}; NMR ($CDCl_3$) δ 2.7–3.1 (m, 2 H), 4.2–4.5 (m, 1 H), 6.5–7.5 (m, 13 H), 7.7–8.0 (m, 2 H); MS (20 eV), *m/e* (relative intensity) 298 (M^+, 2.6), 208 (90), 207 (100), 178 (15). Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.52; H, 6.08; N, 9.38. Found: C, 84.60; H, 6.27; N, 9.11.

The earlier fractions were purified by recrystallization once from ethanol and once from 60–80 °C petroleum ether to give 0.652 g (33%) of **7**, mp 115–117 °C.

The analytical sample (from 60–80 °C petroleum ether) had a melting point of 116–117 °C: IR (KBr) 1490, 1350, 1250, 1170, 750, 690 cm^{-1}; NMR δ 2.7–3.1 (m, 2 H), 4.3–4.6 (m, 1 H), 5.15 (s, 2 H), 6.5–7.5 (m, 17 H), 7.7–8.0 (m, 2 H); MS, *m/e* (relative intensity) 388 (M^+, 0.6), 297 (100), 91 (100). Anal. Calcd for $C_{28}H_{24}N_2$: C, 86.55; H, 6.23; N, 7.21. Found: C, 86.64; H, 6.27; N, 7.33.

Preparation of 1,4-Ethano-1,4-dihydro-3-phenylcinnoline, 8. Dianion **2**, from 1 g (4.85 mmol) of **1**, was treated with 0.4 mL (5 mmol) of 1,2-dichloroethane. The crude reaction product (1.08 g) was chromatographed on silica gel with benzene as eluant. 2-Phenylindole[13] (0.041 g, 5%) eluted first followed by 0.242 g of material that could not be characterized.

The remaining material (0.638 g) was removed from the column and recrystallized from benzene, giving 0.398 g (34%) of **8**, mp 136–137 °C.

Recrystallization from benzene provided an analytical sample: mp 136–137 °C; IR (KBr) 1540, 1470, 1440, 1340, 1160, 1010, 760, 680 cm^{-1}; NMR (acetone-d_6) δ 1.6–2.0 (m, 2 H), 2.7–3.2 (m, 2 H), 4.9 (t, 1 H, J = 3 Hz), 7.1–7.7 (m, 7 H), 7.8–8.2 (m, 2 H); MS, *m/e* (relative intensity) 234 (38, M^+), 233 (16), 131 (45), 130 (100), 129 (13), 103 (43). Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.01; H, 6.03; N, 11.95. Found; C, 81.87; H, 6.04; N, 11.76.

Preparation of 4-(3-Chloropropyl)-1,4-dihydro-3-phenylcinnoline, 9a. Dianion **2**, from 1 g (4.85 mmol) of **1**, was treated with 0.5 mL (5 mmol) of 1,3-dichloropropane. The crude reaction product (1.41 g) was chromatographed on silica gel with benzene as eluant. 2-Phenylindole (63 mg, 7%) eluted first followed by 1.01 g of crude **9** as an oil. This **9** was crystallized from 60–80 °C petroleum ether, giving 0.82 g (59%) of **9**, mp 121–122 °C.

An analytical sample was obtained by recrystallization from 60–80 °C petroleum ether: mp 121–122 °C; IR (KBr) 3380, 1580, 1470, 1360, 1305, 1255, 750 cm^{-1}; NMR (acetone-d_6) δ 1.7–2.0 (m, 4 H), 3.4–3.8 (m, 2 H), 4.3–4.6 (m, 1 H), 6.9–7.6 (m, 7 H), 7.8–8.1 (m, 2 H), 9.4 (s, 1 H, exchanges with D_2O); MS, *m/e* (relative intensity) 286 (^{37}Cl, M^+, 7), 284 (^{35}Cl, M^+, 21), 207 (100), 178 (29). Anal. Calcd for $C_{17}H_{17}N_2Cl$: C, 71.69; H, 6.02; 9.83. Found: C, 71.87; H, 6.13; N, 9.95.

Preparation of 4-(4-Chlorobutyl)-1,4-dihydro-3-phenylcinnoline, 9b. Dianion **2**, prepared from 1.03 g (5 mmol) of **1**, was treated with 0.55 mL (5 mmol) of 1,4-dichlorobutane. The crude reaction product (1.44 g) was chromatographed on silica gel with toluene as eluant. The first fraction (0.79 g) consisted of three different compounds (TLC). This was followed by 0.38 g of **9b**. Rechromatographing the first fraction (silica gel, benzene) separated 0.59 g of **9b** from the other compounds: combined yield 0.96 g (67%), a yellow viscous oil. Repeated attempts to crystallize this material failed: IR (CCl_4) 3400, 1590, 1470, 1310, 1250, 690 cm^{-1}; NMR (acetone-d_6) δ 1.2–2.0 (m, 6 H), 3.48 (t, J = 6 Hz, 2 H), 4.30 (t, J = 6 Hz, 1 H), 6.8–8.0 (m, 9 H), 9.36 (s, 1 H, exchanges with D_2O); MS, *m/e* (relative intensity) 300 (1.6, ^{37}Cl, M^+), 298 (4.7, ^{35}Cl, M^+), 208 (28), 207 (100), 178 (11), 78 (37). Calcd for $C_{18}H_{19}N_2{}^{35}Cl$: 298.1237. Found: 298.1237.

Because of the instability of **9b**, an additional sample was needed at a later date. The above experiment was repeated by using 2.2 mL (20 mmol) of 1,4-dichlorobutane, and the isolated **9b** amounted to 1.17 g (81%).

Preparation of 1,4,4-Tricarbomethoxy-1,4-dihydro-3-phenylcinnoline, 10. Dianion **2**, prepared from 1.03 g (5 mmol) of **1**, was treated with 1.55 mL (20 mmol) of methyl chloroformate. The crude product (1.89 g) was chromatographed on silica gel with methylene chloride as eluant.

The first compound which eluted was **10** (1.03 g). Recrystallization from 4:1 ethanol–60–80 °C petroleum ether provided 0.95 g (51%) of **10**: mp 187–188 °C; IR (KBr) 1730 (br), 1440, 1330, 1280, 1230, 760, 700 cm^{-1}; NMR ($CDCl_3$) δ 3.56 (s, 3 H), 3.59 (s, 3 H), 3.89 (s, 3 H), 7.3–8.0 (m, 9 H); MS, *m/e* (relative intensity) 382 (23, M^+), 324 (21), 323 (100), 280 (20), 279 (94), 176 (12). Anal. Calcd for $C_{20}H_{18}N_2O_6$: C, 62.82; H, 4.75; N, 7.32. Found: C, 62.80; H, 4.81; N, 7.46.

This was followed by 0.30 g of material which could not be resolved into pure components. The remaining material (0.36 g) was removed from the column with methanol. This was recrystallized once from 60–80 °C petroleum ether and once from ethanol to give 0.26 g (20%) of **15**: mp 213–214 °C; IR (KBr) 1710, 1440, 1350, 1290, 1240, 1060, 750 cm^{-1}; NMR (acetone-d_6) δ 3.82 (s, 3 H), 3.84 (s, 3 H), 4.54 (s, 1 H), 4.63 (s, 1 H), 6.7–8.2 (m, 18 H); MS, *m/e* (relative intensity) 266 (43), 265 (100, $M^+/2$), 221 (79), 207 (35), 206 (46), 178 (73). Anal. Calcd for $C_{32}H_{26}N_4O_4$: C, 72.44; H, 4.94; N, 10.56. Found: C, 72.28; H, 5.00; N, 10.56.

Registry No. **1**, 10604-22-5; **2**, 86785-49-1; **4a**, 10604-23-6; **4b**, 86785-50-4; **5**, 86785-51-5; **6**, 86785-52-6; **7**, 86785-53-7; **8**, 86785-54-8; **9a**, 86785-55-9; **9b**, 86785-56-0; **10**, 86785-57-1; **15**, 86785-58-2; 2-phenylindole, 948-65-2; 1,4-dichlorobutane, 110-56-5.

Nuclear Magnetic Resonance Studies of Methylsilver(I) Complexes

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Received September 8, 1982

Methylsilver(I) complexes have been studied by ^1H, ^7Li, ^{13}C, and ^{31}P NMR spectroscopy, and structural information about the methylsilver(I), lithium dimethylsilver(I), and dilithium trimethylsilver(I) complexes has been obtained. Possible structures of these complexes are discussed in terms of the results of these multinuclear NMR studies. Variable-temperature NMR of these complexes has also been studied. These NMR studies show that intermolecular exchange of methyl groups occurs for each of these complexes. The activation parameters for these exchange processes were determined from line-shape analysis of the dynamic ^{13}C NMR spectra of these complexes.

Multinuclear NMR has proven to be a powerful tool for the examination of the structures of and the dynamic processes for a variety of organometallic compounds.[1] Here we describe the results of variable-temperature ^1H

0276-7333/83/2302-1354$01.50/0

and ^{13}C NMR spectroscopy experiments on methylsilver(I) complexes containing tri-*n*-butylphosphine, methyllithium, and/or lithium iodide in various solvents. In these experiments, the propitious magnetic properties of silver (two equally abundant isotopes each with a spin of $^1/_2$) provides an excellent method for studying the dynamics and structures of these thermally unstable organometallic species. The multinuclear NMR spectroscopy experiments described here unambiguously exclude certain possible structures for these organometallic compounds in solution and, additionally, establish that intermolecular exchange of methyl groups between methylsilver(I) complexes is faster than intramolecular methyl group exchange within putative methylsilver(I) aggregates. The results of these NMR studies of alkylsilver(I) species are also contrasted with related structural and DNMR studies in alkylcopper(I), alkylgold(I), arylsilver(I), and alkyllithium reagents.[1-4]

Table I. Chemical Shift Data for Methylsilver(I) Complexes at -80 °C[a]

obsd nucleus	solv	methylsilver(I) complex 1	2	3
^1H (methyl)	$(C_2H_5)_2O$	−0.69	−1.15	*b*
^{13}C (methyl)	$(C_2H_5)_2O$	−8.80[c]	−9.68[d]	−9.13
	$(C_2H_5)_2O$	−9.14[e]	−9.6[e]	*b*
	$C_6H_5CH_3$	−6.97	−8.24	*b*
^{31}P	$(C_2H_5)_2O$	−6.66	−22.4	−32.6[f]
	$(C_2H_5)_2O$	−6.88[e]	−26.6[e]	*b*
	$C_6H_5CH_3$	−6.85	*b*	*b*
^7Li	$(C_2H_5)_2O$	−2.7	−3.0[g]	−3.1[h]

[a] NMR spectra obtained by using ca. 0.15 M solutions prepared according to eq 1–3 using 10% benzene-d_6 as an internal lock with shifts reported in ppm relative to Me_4Si (^1H and ^{13}C), external 85% H_3PO_4 (^{31}P), or external aqueous 26% LiBr (^7Li). These chemical shifts were unaffected when benzene-d_6 was used as an external lock (see text discussion). [b] This chemical shift was not measured in these studies. [c] In a 1.1 M solution this chemical shift was δ -8.15. [d] In a 0.63 M solution this chemical shift was δ -9.06. [e] Less than 0.01 M (less than 0.1 equiv of halide/silver) lithium halide was present. [f] This absorption was coincident with that of tri-*n*-butylphosphine under the same conditions. [g] This broad peak had a shoulder at ca. δ -2.7. [h] This broad peak had shoulders at ca. δ -2.7 and -3.3. An additional absorption absorption at δ -0.7 coincident with that of methyllithium was also present in these spectra.

Table II. Carbon–Silver, Proton–Silver, and Phosphorus–Silver Coupling Constants for Methylsilver(I) Complexes in Various Solvents[a]

obsd ^1J coupling	solv	methylsilver(I) complex 1	2
$^{107}Ag-^{13}C$	$(C_2H_5)_2O$	129.5	85.5
$^{109}Ag-^{13}C$	$(C_2H_5)_2O$	149.6	98.2
$^{107}Ag-^{13}C$	$(C_2H_5)_2O$[b]	130.6	86.1
$^{109}Ag-^{13}C$	$(C_2H_5)_2O$[b]	148.9	99.6
$^{107}Ag-^{13}C$	$(C_2H_5)_2O$[c]	129.1	85.6
$^{109}Ag-^{13}C$	$(C_2H_5)_2O$[c]	150.1	99.0
$^{107}Ag-^{13}C$	$C_6H_5CH_3$	128.6	83.8
$^{109}Ag-^{13}C$	$C_6H_5CH_3$	149.4	95.5
$^{107,109}Ag-^1H$[d,f]	$(C_2H_5)_2O$	10.8	6.0
$^{107}Ag-^{31}P$	$(C_2H_5)_2O$	275.6	*e*
$^{109}Ag-^{31}P$	$(C_2H_5)_2O$	316.5	*e*
$^{107}Ag-^{31}P$	$(C_2H_5)_2O$[c]	278.5	*e*
$^{109}Ag-^{31}P$	$(C_2H_5)_2O$[c]	317.7	*e*
$^{107,109}Ag-^{31}P$[d]	$(C_2H_5)_2O$[b]	296	*e*
$^{107}Ag-^{31}P$	$C_6H_5CH_3$	278.9	*e*
$^{109}Ag-^{31}P$	$C_6H_5CH_3$	321.6	*e*

[a] Coupling constants (±1 Hz) in hertz determined from NMR spectra of ca. 0.15 M solutions of 1 and 2 prepared according to eq 1 and 2, respectively, in the indicated solvent at -70 °C (ca. 10% benzene-d_6 was present as an internal lock unless otherwise indicated). [b] This solution contained less than 0.01 M lithium halide (less than 0.1 equiv of halide/silver). [c] External benzene-d_6 was used as a lock. [d] The $^{107,109}Ag$ couplings were not resolved. [e] No coupling was observed. [f] ^2J coupling.

Characterization of (tri-*n*-butylphosphine)methylsilver(I) (**1**) formed by the addition of 1 equiv of methyllithium to 1 equiv of tetrakis((tri-*n*-butylphosphine)-iodosilver(I)) (**4**) (eq 1) by ^{13}C and ^{31}P NMR spectroscopy

$$^1/_4\{LiCH_3\}_4 + \underset{\mathbf{4}}{^1/_4\{IAgP(n\text{-}C_4H_9)_3\}_4} \xrightarrow[-78\ °C]{Et_2O} \underset{\mathbf{1}}{CH_3AgP(n\text{-}C_4H_9)_3} + LiI \quad (1)$$

has already been reported.[5] Likewise, ^{13}C NMR spectroscopy has been used to characterize lithium dimethylsilver(I) (**2**) and dilithium trimethylsilver(I) (**3**) (formed in eq 2 and 3, respectively). Complex **3** is formed

$$2^1/_4\{LiCH_3\}_4 + \underset{\mathbf{4}}{^1/_4\{IAgP(n\text{-}C_4H_9)_3\}_4} \xrightarrow[-78\ °C]{Et_2O} \underset{\mathbf{2}}{Li(CH_3)_2Ag} + P(n\text{-}C_4H_9)_3 + LiI \quad (2)$$

$$3^1/_4\{LiCH_3\}_4 + \mathbf{4} \xrightarrow[-78\ °C]{Et_2O} \underset{\mathbf{2}}{Li(CH_3)_2Ag} + P(n\text{-}C_4H_9)_3 + {}^1/_4\{LiCH_3\}_4 + LiI \rightleftharpoons \underset{\mathbf{3}}{Li_2(CH_3)_3Ag} + LiI + P(n\text{-}C_4H_9)_3 \quad (3)$$

as part of an equilibrium mixture of **3**, **2**, and methyllithium. The equilibrium constant for formation of **3** from **2** and methyllithium was determined to be 0.015 from ^{13}C NMR spectroscopy experiments in which 3:1, 5:1, and 9:1 ratios of methyllithium and **4** were added together. The relative amounts of **2**, **3**, and methyllithium in these experiments were estimated on the basis of the areas of the peaks ascribable to each of these components of the equilibrium mixture without correction for possible variances in relaxation times or NOE's of the various species. We have also examined ^1H and ^7Li NMR spectra of **1**, **2**, and **3**. The ^1H NMR spectra of **1** and **2** both showed coupling to silver, but the $^1H-^{109}Ag$ and $^1H-^{107}Ag$ couplings were not resolved and only two peaks were seen. ^1H NMR was not useful for studies of **3** since solutions known to contain **3** by ^{13}C NMR spectroscopy were indistinguishable by ^1H NMR from simple overlapping of the individual spectra of **2** and methyllithium. The ^7Li NMR spectrum of **1** was identical with the ^7Li NMR spectrum of lithium iodide. ^7Li NMR spectra of solutions of **2** containing lithium iodide contained an unsymmetrical broad peak centered at ca. δ −3.0 (relative to external 26% aqueous lithium bromide) with an upfield shoulder at ca. δ −2.7

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[1] Harris, R. K., Mann, B. E., Eds. "NMR and the Periodic Table"; Academic Press: New York, 1978.

[2] Structural characterization of related alkylcopper(I) ate complexes by ^1H NMR, X-ray scattering, and kinetic techniques have been reported: cf. (a) Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 5312–5317. (b) Pearson, R. G.; Gregory, C. D. *Ibid.* **1976**, *98*, 4098–4104. (c) San Filippo, J., Jr. *Inorg. Chem.* **1978**, *17*, 275–283.

[3] Rice, G. W.; Tobias, R. S. *Inorg. Chem.* **1976**, *15*, 489–490 and references therein.

[4] (a) ten Hoedt, R. W. M.; van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1979**, *179*, 227–240. (b) van Koten, G.; Noltes, J. G. *Ibid.* **1979**, *174*, 367–387. (c) Blenkers, J.; Hofstee, H. K.; Boersma, J.; van der Kerk, G. J. M. *Ibid.* **1979**, *168*, 251–258.

[5] Bergbreiter, D. E.; Lynch, T. J. *J. Org. Chem.* **1981**, *46*, 727–733.

(coincident with LiI under similar conditions). ^{7}Li NMR spectroscopy of solutions prepared according to eq 3 that should have contained **2**, **3**, LiI, and methyllithium consisted of two well-separated peaks. One peak at δ −0.7 was coincident with that of methyllithium under similar conditions. The other broader peak was upfield and centered at ca. δ −3.1 with small poorly resolved shoulders on both the upfield and downfield sides.

No evidence for methylsilver(I) complexes other than **1**, **2**, and **3** was obtained in any of these NMR spectroscopy experiments. The results of these experiments are summarized in Tables I and II, and the implications of the NMR data in Tables I and II along with some additional studies and importance of these results to possible structures of these complexes are discussed further below.

Solution structures of Methylsilver(I) Complexes. The structures of a number of σ-bonded aryl and alkynyl organometallic compounds of the group 1B metals have been determined by NMR and X-ray techniques.[6-9] The propensity of these metals is to form complexes with multicenter bonds as is illustrated by the recently described arylcopper(I) compound $(Cu_5(C_6H_5)_6)Li$ and by the extensive studies of van Koten and Noltes.[6,10] In contrast, the structures of the σ-bonded alkyls of copper(I), silver(I), and gold have not been as well-defined. For example, the structure of the synthetically important methylcuprates has been the subject of some contention and both planar and tetrahedral structures have been proposed.[2b,11] An octahedral arrangement has been suggested as a likely structure for *n*-butylcuprates.[2c] However, the permethylaurates (gold(I) and gold(III)), unlike alkylcopper(I) compounds, evidently exist in solution as ion pairs with discrete dimethylaurate and tetramethylaurate units.[3] Alkylsilver(I) compounds' solution structures have not previously been determined.

The results of our NMR studies described above and in Tables I and II place some important limitations on possible solution structures for methylsilver(I) complexes **1**, **2**, and **3** and further serve to differentiate them from qualitatively similar arylsilver(I) species whose structures are known. First, there is no evidence in any of our studies for ^{7}Li–^{13}C coupling in any methylsilver(I) compound even at −80 °C. ^{7}Li–^{13}C coupling was reported previously for arylsilver(I) complexes.[4,7,10] This absence of ^{7}Li–^{13}C coupling in **1**, **2**, and **3** is most easily explained by assuming that there is no covalent bonding between lithium and a methyl group in these methylsilver(I) complexes. However, the ^{7}Li–^{13}C coupling could also be too small to detect (the reported ^{7}Li–^{13}C coupling seen in arylsilver(I) complexes was <10 Hz) or could have been washed out by fast quadrupolar relaxation of ^{7}Li ($I = {}^{3}/_{2}$). Fast intra- or intermolecular exchange of methyl groups could also obscure such coupling, but this explanation is unlikely in view of our observations of ^{13}C and ^{1}H coupling to ^{107,109}Ag at low temperature (−80 °C). The question of lithium or lithium iodide incorporation in **1**, **2**, or **3** is more problematic. The observed ^{7}Li NMR spectra (vide supra) suggest that lithium iodide is present in solutions of **1**, **2**, and **3** and that lithium iodide is not quantitatively incorporated into aggregates with these species since ^{7}Li NMR spectra contained a peak or a shoulder ascribable to lithium iodide. The implication that lithium iodide is not an integral part of **1** and **2** is supported by experiments in which low halide solutions of **1** and **2** were examined by ^{13}C and ^{31}P NMR spectroscopy. In these experiments, methylsilver(I) complexes **1** and **2** were prepared from chlorosilver(tri-*n*-butylphosphine) and low halide methyllithium and lithium chloride produced in these metalations was precipitated with dioxane. While the resulting solutions still contained a small amount of halide as lithium chloride (<10% of the total halide remained in solution in these experiments), the observation that the ^{13}C and ^{31}P chemical shifts and ^{107,109}Ag–^{13}C and ^{107,109}Ag–^{31}P coupling constants were essentially identical in **1** (see Table II) and that the ^{13}C chemical shifts and coupling constants were also unchanged in **2** is good evidence that lithium iodide is not a part of the structure of **1** or **2**. Unavoidable coprecipitation of **2** with lithium chloride rendered similar experiments for **3** impractical.

Lithium halides such as lithium bromide have been reported to significantly affect the thermal stability of alkylsilver(I) species in tetrahydrofuran–hexamethylphosphoramide (THF–HMPA) solutions.[12] Magnesium halides are also evidently influential in determining the course of similar thermal decompositions in ether although lithium halides have little influence on the reaction's course in this solvent.[13] Thus, although the NMR studies described here in diethyl ether solutions suggest limited or no involvement of lithium iodide in the structures of **1** and **2**, this situation may not necessarily obtain with other halides or in other solvents.

A second important limitation on possible structures for **1**, **2**, and **3** based on these NMR experiments is that neither the methyl groups in **1**, **2**, or **3** nor the phosphine groups in **1** are bonded to more than one silver(I) atom. This conclusion is based on the observation of two doublets in the ^{13}C NMR spectra of **1**, **2**, and **3** arising from ^{13}C–^{107}Ag and ^{13}C–^{109}Ag coupling (cf. Table II and Figure 1). The ratio of these two different C–Ag coupling constants was in every case equal to the expected ratio of gyromagnetic ratios of ^{107}Ag and ^{109}Ag ($\gamma_{^{107}Ag}/\gamma_{^{109}Ag} = 0.87$). Higher order multiplets would have been expected in these NMR spectra if the methyl groups had been attached to two or more silver atoms ($I = {}^{1}/_{2}$ for Ag). Bridging of a phosphine ligand between two silver atoms in **1** is similarly precluded by the observation of two doublets in the ^{31}P NMR of **1** that were characteristic of the splitting of phosphorus by one silver atom (Tables I and II).

A third constraint on structures for **1**, **2**, and **3** is that all the methyl groups in each of these individual species are equivalent by ^{13}C NMR spectroscopy. Variable-temperature NMR experiments described below have shown that this observed equivalence is not the result of fast exchange. This specifically excludes aggregated structures similar to those proposed to methylcuprates[11] having a tetrahedral arrangement of two lithiums and two silvers with methyl groups on each face.

Finally, we were unable to detect virtual coupling of $^{13}CH_3$ groups to other silver atoms in any of these structures. Such virtual coupling would have been good evidence for aggregation, but its absence may not be as significant. ^{31}P NMR spectra of various trialkyl- or triarylphosphine complexes of silver(I) that are known to be

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(6) Edwards, P. G.; Gellert, R. W.; Marks, M. W.; Bau, R. *J. Am. Chem. Soc.* **1982**, *104*, 2072–2073.

(7) ten Hoedt, R. W. M.; Noltes, J. G.; van Koten, G.; Sepk, A. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1800–1806.

(8) Jarvis, J. A. J.; Kilbourn, B. T.; Pearce, F.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 475–476.

(9) Blake, D.; Calvin, G.; Coates, G. E. *Proc. Chem. Soc.* **1959**, 396–397.

(10) van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1979**, *101*, 6593–6599 and references therein.

(11) House, H. O.; Umen, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 5495–5497.

(12) Westmijze, H.; Kleijn, H.; Vermeer, P. *J. Organomet. Chem.* **1979**, *172*, 377–383.

(13) Whitesides, G. M.; Bergbreiter, D. E.; Kendall, P. E. *J. Am. Chem. Soc.* **1974**, *96*, 2806–2813.

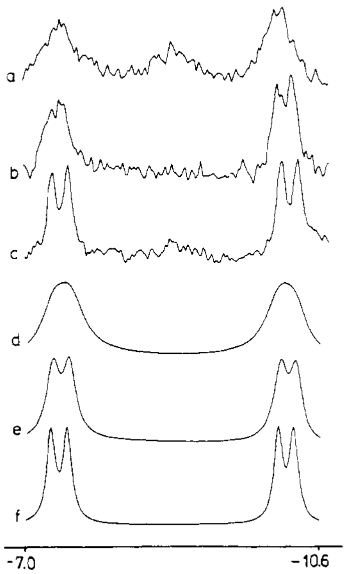


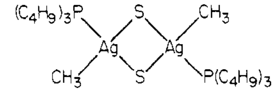
Figure 1. Experimental and calculated ^{13}C NMR spectra of 0.1 M ether solutions of 1 (containing 10% benzene-d_6) at 50.3 MHz in the region δ -7.0 to -10.6 at various temperatures: (a) -44 °C; (b) -59 °C; (c) -69 °C; (d) k = 90 s^{-1}; (e) k = 30 s^{-1}; (f) k = 10 s^{-1}.

tetrameric in THF also do not exhibit virtual coupling.[14-16]

Possible structures for 1 that are in accord with our spectroscopic data include 5 and 6. Higher order sol-

$CH_3AgP(C_4H_9)_3$

5



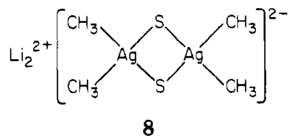
6

vent-bridged aggregates would also be possible. However, bridging methyl groups, phosphine ligands, or lithium halide would all seem unlikely in view of the NMR data described above. In the structures below, "S" represents solvent.

Possible structures for 2 that are in accord with our spectroscopic data would be similar to those described above. Reasonable structures might include 7 or 8.

$Li^+((CH_3)_2Ag)^-$

7



8

Neither of these structures contains a tri-n-butylphosphine ligand directly bonded to silver. However, ^{31}P NMR spectroscopy of solutions of 2 at -80 °C in diethyl ether did contain a single broad peak at δ -26.6 (relative to external 85% H_3PO_4) while free tri-n-butylphosphine is a singlet at δ -32.6 under similar conditions. The observed chemical shift in the ^{31}P NMR spectrum we believe results from the presence of some phosphine complexed 2 that is undergoing rapid exchange of its phosphine ligand with phosphine-free 2 and uncomplexed tri-n-butylphosphine.

The ^{13}C NMR spectrum of 3 has shown that 3 is present in equilibrium with 2 and methyllithium and that it consists of three equivalent nonbridging methyl groups that are bonded to a single silver atom. Coordination of tri-n-butylphosphine that is present in solutions of 3 to silver evidently does not occur. The ^{31}P NMR spectrum of 3 is identical with the ^{31}P NMR spectrum of pure tri-n-butylphosphine having a single peak at δ -32.6 at -80 °C. With 16 electrons and a high formal negative charge, 3 is the most likely of these methylsilver(I) complexes to be monomeric in solution and probably exists as an ion pair in analogy to the methylaurate(I) complexes.[3]

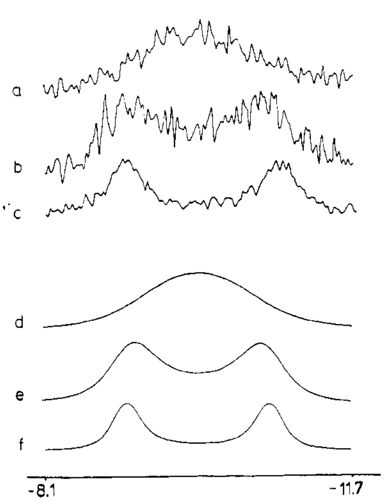


Figure 2. Experimental and calculated ^{13}C NMR spectra of 0.1 M ether solutions of 2 (containing 10% benzene-d_6) at 50.3 MHz in the region δ -8.1 to -11.7 at various temperatures: (a) -10 °C; (b) -19 °C; (c) -29 °C; (d) k = 917 s^{-1}; (e) k = 400 s^{-1}; (f) k = 184 s^{-1}.

All of the above data and discussion refer to results obtained in diethyl ether solutions containing 10–15% of benzene-d_6 as an internal lock for NMR purposes. We have briefly examined benzene-free ether solutions and toluene solutions of 1 and 2 and verified that our results obtain in other solvent systems. There was no effect either on the chemical shifts of the $^{13}CH_3$ groups of 1 or 2, on the ^{31}P chemical shift of 1, or on any of the ^{13}C–$^{107,109}Ag$ or ^{31}P–$^{107,109}Ag$ coupling constants when spectra were obtained in the absence of benzene-d_6 in diethyl ether. The chemical shifts varied by less than 2.5 ppm and the coupling constants were essentially the same. The evident lack of influence of benzene-d_6 on these spectra was not unexpected however since it was unlikely that benzene-d_6 would compete effectively against tri-n-butylphosphine for coordination to silver(I). To further establish that our observations are not limited only to ether solvents and to show what solvent effects might have been expected if benzene-d_6 were the only solvent in the coordination sphere of these complexes, we also obtained spectra of 1 and 2 in toluene. This solvent change did alter the chemical shifts but not the coupling constants of 1 and 2. The changes are noted in Tables I and II. Such effects would be consistent with any of the above suggested structures for 1 and 2 (5–8) and could be due to either differing coordination of solvent or merely to differences in the solvents' polarity.

Although the above NMR data cannot unambiguously distinguish between the various possible structures for 1, 2, and 3 in solution, these data do demonstrate that methylsilver(I) reagents differ from their better characterized arylsilver(I) counterparts. These differences may reflect the differing bridging ability of aryl groups vs. methyl groups. In any case, the results of structural studies of arylsilver(I) reagents are apparently not universally applicable to structural questions posed by other organosilver(I) compounds.

Dynamic Nuclear Magnetic Resonance (DNMR) Spectroscopy of Methylsilver(I) Complexes. We have

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[14] Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386–6391.

[15] Aggregation of $(IAgP(n\text{-}C_4H_9)_3)_4$ and $(IAgP(C_2H_5)_3)_4$ in THF has been verified in our laboratories under conditions where ^{31}P NMR studies of these complexes show simple pairs of doublets for ^{31}P–$^{107,109}Ag$ coupling: Shimazu, S.; Bergbreiter, D. E., unpublished results.

[16] Mann, F. G.; Wells, A.; Purdie, D. *J. Chem. Soc.* **1937**, 1828–1836.

Table III. Activation Parameters of Exchange Processes for Methylsilver(I) Complexes

complex[a]	temp, °C	k, s^{-1}	$\Delta G^{\ddagger}_{25\,°C}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a, kcal/mol
methyllithium:4						
1:1 (**1**)	−69	10 ± 7%	12.4 ± 0.6	7.5 ± 0.3	−16 ± 2	7.9 ± 0.3
	−59	30 ± 20%				
	−44	90 ± 16%				
2:1 (**2**)	−29	184 ± 20%	11.9 ± 1.0	10.7 ± 0.8	−4 ± 3	11.2 ± 0.8
	−19	400 ± 5%				
	−10	917 ± 8%				
3:1 (**3**)	−44	42 ± 25%	11.5 ± 0.9	11.7 ± 0.6	0.4 ± 2.4	12.1 ± 0.6
	−37	96 ± 20%				
	−29	210 ± 14%				

[a] Methylsilver(I) complexes were prepared according to eq 1–3 as 0.1 M solutions in diethyl ether containing 10% benzene-d_6.

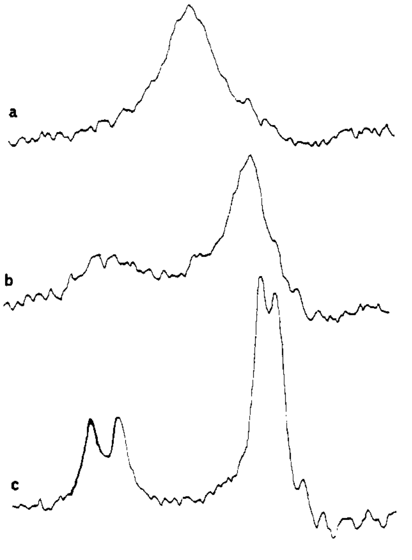

Figure 3. Variable-temperature ^{1}H NMR spectra at 200 MHz of a 1.5:1 mixture of methyllithium and **4** in diethyl ether (containing 10% benzene-d_6) showing only **1** at δ −0.69 and **2** at δ −1.15: (a) −40 °C; (b) −60 °C; (c) −80 °C.

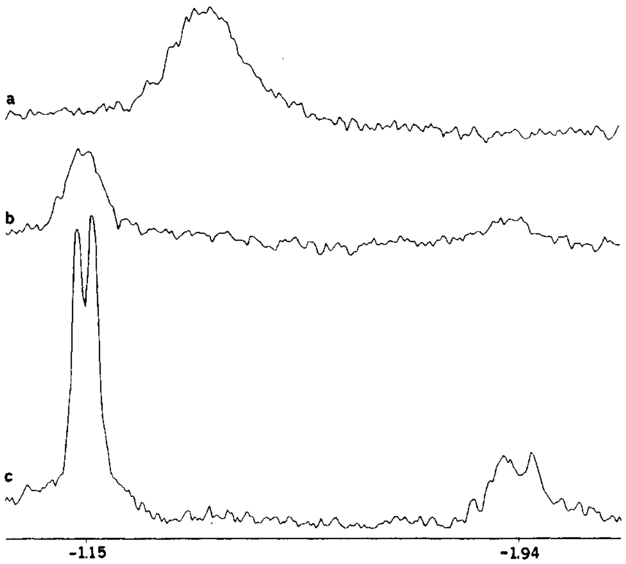

Figure 4. Variable-temperature ^{1}H NMR spectra at 200 MHz of a 3:1 mixture of methyllithium and **4** in diethyl ether (containing 10% benzene-d_6) showing only **2** at δ −1.15 and methyllithium at δ −1.94: (a) +20 °C; (b) −20 °C; (c) −80 °C. A separate absorption for **3** that was known to be present was not detectable by ^{1}H NMR although **3** was detectable by ^{13}C NMR spectroscopy.

performed variable-temperature ^{13}C and ^{1}H NMR studies on **1**, **2**, and **3** and methyllithium and on admixtures of these complexes in order to gain some insight from the resulting dynamic phenomena about the structure and bonding in these alkylsilver(I) reagents.[17,18] The coalescence of the ^{13}C NMR spectra of **1** and **2** (Figures 1 and 2, respectively) is the result of the loss of ^{13}C–^{107,109}Ag coupling. This loss of ^{13}C–^{107,109}Ag coupling is due to exchange of methyl groups from one silver atom to another in an intermolecular sense. This intermolecularity is evidenced by the decreased multiplicity seen in the higher temperature spectra. If exchange of methyl groups from one silver atom to another had occurred in an intramolecular sense, increased rather than decreased multiplicity would have been seen in the high-temperature spectra where fast exchange is occurring. For example, if intramolecular exchange had occurred in a dimeric complex, the high-temperature spectra should have contained three sets of three lines rather than the observed broad single peak seen in Figure 2. Coalescence behavior of **1** and **2** (Figure 3) or of **2** and methyllithium (Figure 4) seen in the ^{1}H NMR spectra also support this conclusion.[19,20]

Figures 1 and 2 show in addition to the experimental spectra, calculated spectra which were used to determine the rate constants of methyl exchange at several temperatures (Table III). The calculated spectra were generated by using the computer program DNMR3.[21,22] The ^{13}C–

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[17] Applications include both intra- and intermolecular exchange processes; cf. Adams, R. D.; Cotton, F. A. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 12. Jesson, J. P.; Muetterties, E. L. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 8.

[18] Lambert, J. B.; Shurvell, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. H. "Organic Structural Analysis"; Macmillan: New York, 1976; pp 116–134. Becker, E. E. "High Resolution NMR", 2nd Ed.; Academic Press: New York, 1980; pp 240–252.

[19] Intermolecular exchange is known to be faster than intramolecular exchange in the case of aggregates involving alkyllithium reagents: cf. Brown, T. L. *Acc. Chem. Res.* **1968**, *1*, 23–32.

[20] Variable-temperature ^{13}C NMR spectra of a ca. 0.7 M ether solution of **2** (containing 10% benzene-d_6) at 50.3 MHz showed that the coalescence phenomena occurred at ca. 20 °C lower temperature, indicating that exchange in more concentrated solutions of **2** was 5–10 times faster. Since we have not carried out the more extensive rate–concentration studies and/or studies of the effect of concentration on aggregation that would be necessary to determine the nature of the rate-determining step of these exchange reactions (e.g., dissociation of an aggregate, exchange between aggregates, exchange between monomers or some combination of these processes), the observed rate increase at higher concentration of **2** is consistent with but is not unambiguous evidence for the proposed intermolecularity of the exchange phenomena. The observed changes in multiplicity seen in Figures 1–4 are on the other hand unambiguous evidence for the intermolecularity of the exchange process although they do not establish the exact nature of the rate-determining step in this exchange of methyl groups between silver atoms in **1**, **2**, and **3**.

[21] Binsch, G. *J. Am. Chem. Soc.* **1969**, *91*, 1304–1309.

^{107,109}Ag couplings were treated by assuming that the pair of doublets in the ^{13}C NMR arose from the resonance of chemically different carbon atoms that were allowed to exchange. This simplification is valid when the difference in chemical shifts of the coupled nuclei in hertz is much greater than the coupling constant (i.e., $\Delta\nu > 10$ J).[23] This restriction holds true in our case since $\Delta\nu$ was 42 MHz and J was ca. 100 Hz.

The rate constants originally obtained from the calculated spectra (k') were corrected for the number of methyl groups on a complex and for the fact that statistically an exchanging methyl group had a 50% chance of bonding to another silver(I) atom with the same field alignment as the silver(I) atom to which it was previously bound. For example, the original rate constant for the exchanging **3** complex at −29 °C was multiplied by 6 (i.e., $k' \times 3 \times 2 = 210$ s^{-1}) to obtain the rate constant that was used in the calculation of the activation parameters. Error limits for the rate constants were determined by determining rate constants which gave visually different simulated spectra. Errors in the temperature were assumed to be ±2 °C.

The rate constants and associated temperatures were used in the calculation of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and E_a using the computer program EXEN.[24] These data are listed in Table III. Free energies of activation for exchange processes for all of these methylsilver(I) complexes are quite similar. The enthalpy of activation for exchange in **1** is slightly lower and the activation entropy is more negative. However in the absence of more detailed structural and mechanistic studies, we have chosen to not speculate further about the way in which these exchange reactions might be occurring.

Experimental Section

General Methods. The NMR spectrometers used to collect data were a Varian FT-80 (^{31}P, ^{7}Li, and ^{13}C NMR spectra), a JEOL PFT-100 (^{31}P NMR spectra), and a Varian XL-200 (^{1}H and ^{13}C NMR spectra) spectrometer. Samples for the NMR experiments were prepared both in tubes that were fitted with septa and flushed with nitrogen and in sealed NMR tubes under nitrogen. Benzene-d_6 (10–15% of solvent) was used as an internal lock. When benzene-d_6 was to be excluded from the system, lock was maintained by using benzene-d_6 contained in a concentric capillary within the sample tube containing the organometallic solution of interest. ^{1}H and ^{13}C chemical shifts are reported with respect to benzene (δ 7.15 (^{1}H) and δ 128.0 (^{13}C)). ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4 and ^{7}Li NMR chemical shifts are relative to external 26% aqueous lithium bromide. The temperature measurements of the JEOL PFT-100 and Varian FT-80 NMR spectrometers were made by placing a thermocouple into a temperature-equilibrated NMR tube containing ether while the tube was in the NMR spectrometer probe. The Varian XL-200 instrument was equipped with a thermocouple in the NMR probe which was used for temperature measurement.

Lithium$_{n-1}$ (Tri-*n*-butylphosphine)(methyl)$_n$silver(I) (*n* = 1, 2, or 3 for 1, 2, or 3, Respectively). Samples used in NMR studies were prepared as ether–benzene-d_6 solutions in the same manner as their corresponding *n*-butylsilver(I) complexes by substitution of methyllithium for *n*-butyllithium.[5] The 50% ^{13}C-enriched methyllithium for the ^{13}C NMR studies was prepared from 90% ^{13}C-enriched methyl iodide (KOR Inc.) and *n*-butyllithium following the method of McKeever.[25] Samples prepared from **4** contained lithium iodide from the starting iodosilver(I) complex. Halide free samples were obtained by using chloro(tri-*n*-butylphosphine)silver(I) as a silver(I) precursor and precipitating the lithium chloride byproduct as a complex with dioxane. Halide-free samples prepared in this way contained less than 0.1 equiv of halide in solution/1.0 equiv of silver(I) as determined by separate analysis of both the solution and dioxanate precipitate.[26] In one case, a $^{13}CH_3OLi$ impurity (resulting from a minor amount of $^{13}CH_3OH$ in the methyl iodide) was present in solutions of **2**. However, this latter impurity had no effect on the NMR studies as verified by additional NMR experiments with **2** that did not contain this impurity.

Solutions for ^{7}Li, ^{13}C, and ^{31}P NMR studies were prepared directly in 10-mm o.d. NMR tubes. In a typical procedure, **2** was prepared by the addition of 1 equiv of **4** (0.087 g, 0.2 mmol) to an oven-dried NMR tube that was immediately sealed with a septum cap and flushed with nitrogen for 5 min. Dry ether (1.5 mL) and benzene-d_6 (0.2 mL) that had been stored over molecular sieves were added to the NMR tube, and the silver complex was dissolved by swirling with a Vortex stirrer. The resulting solution was cooled to −78 °C while under a constant nitrogen pressure. The methyllithium (0.26 mL, 1.53 N) was then added by syringe along the side of the −78 °C tube while the tube was periodically swirled to obtain a clear and colorless solution. Samples were prepared within 12 h of the NMR experiments. Older, partly decomposed samples typically gave more poorly resolved spectra.

Methylsilver(I) samples for ^{1}H NMR experiments were prepared in 40-mL centrifuge tubes and then transferred by forced siphon through a precooled cannula into a dry, −78 °C, septum-capped, and nitrogen-flushed 5-mm o.d. NMR tube. In order to precool the cannula for such transfers, cold nitrogen that was over the methylsilver(I) solution was flushed through the cannula first. When the metal cannula had visibly cooled, the solution of thermally labile methylsilver could be transferred with minimal decomposition.

Acknowledgment. Support of this research by the Robert A. Welch Foundation is gratefully acknowledged.

Registry No. **1**, 52543-56-3; **2**, 76011-10-4; **3**, 76011-11-5; **4**, 28282-03-3; $LiCH_3$, 917-54-4.

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(22) Theoretical line shapes for the ^{13}C NMR spectra of **1** and **2** were calculated by the following program: Kleier, D. A.; Binsch, G. "A Computer Program for the Calculation of Complex Exchange-Broadened NMR Spectra", Program 165; Quantum Chemistry Program Exchange: Indiana University, 1969. The theoretical line shapes for the ^{13}C NMR spectra of **3** were calculated by using a program developed by: Whitesides, G. M.; Fleming, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 2855–2859.

(23) Loewenstein, A.; Connor, T. M. *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 280–295.

(24) (a) EXEN was included in Whitesides' program.[22] (b) The errors in the activation parameters were the standard deviations calculated by EXEN from the estimated errors in the temperature and rate constants. The actual errors, especially in $\Delta S^{\ddagger}$ are often larger: cf. Carlson, E. H. Ph.D. Dissertation, Wayne State University, Detroit, MI 1973.

(25) McKeever, L. D.; Waack, R.; Doran, M. A.; Baker, E. B. *J. Am. Chem. Soc.* **1969**, *91*, 1057–1061.

(26) Titration of chloride was carried out by using Mohr's method: cf. Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. "Quantitative Chemical Analysis", 4th ed.; Macmillan: New York, 1969; pp 719–720.