various π MO's are *identical* in the neutral molecule and in the dianion. Under these circumstances, the difference in calculated $\chi_{\perp}{}^{\pi(L)}$ values between a given neutral molecule and its dianion is attributable solely to the fact that the dianion has one more doubly occupied orbital than the neutral molecule. There are thus consequential (and dramatic) changes in the HOMO-LUMO separation on which, according to Van Vleck's expression,[40] the diamagnetic/paramagnetic nature of the species in question sensitively depends.[7d] This is certainly borne out by the figures presented in Table V.

(6) When the non-London π contributions, $\chi_{\perp}{}^{\pi(\text{non-L})}$, and the σ contributions, $\chi_{\perp}{}^{\sigma}$, to $\chi_{\perp}$ are taken into account, the overall quantities $\chi_{\perp}$ $(\equiv\chi_{\perp}{}^{\pi(L)} + \chi_{\perp}{}^{\pi(\text{non-L})} + \chi_{\perp}{}^{\sigma})$ for I-III are all expected to be diamagnetic. This is true even of III, the $\chi_{\perp}{}^{\pi(L)}$ of which is predicted by methods 4 and 6 to be strongly paramagnetic. If, therefore, crystals of I-III could be obtained and the components of the susceptibility tensors perpendicular to their respective planes could be measured experimentally, the present calculations anticipate that these would all turn out to be diamagnetic. In practice, however, it is unlikely that this experimental feat will be easily achieved in the near future, and it seems most likely that I-III, as they are synthesised, will be studied by means of solution ^{1}H NMR spectroscopy.[25] In the context of this technique, it is the London (or "ring current") contribution which dominates the appearance of the resulting ^{1}H NMR spectra, via its influence on relative ^{1}H NMR chemical shifts (although it should be borne in mind that the nonuniform π-electron charge density extant in these nonalternant systems, and particularly in their dianions, can have an equally important effect on relative ^{1}H NMR shielding).[41] By considering the results of the two "best" methods of calculation (4 and 6) presented in Tables IV and V, we would predict the *paramagnetic* (i.e., shielding) "ring-current" contributions to intramolecular ^{1}H NMR chemical shifts[42] in I-III to be in the order III > II > I. The dianions of I-III are all expected to exhibit "normal" diamagnetic "ring-current" effects similar to those characteristic of the condensed, benzenoid hydrocarbons.

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(40) J. H. Van Vleck, "Electric and Magnetic Susceptibilities", Oxford University Press, Oxford, 1932.

(41) (a) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 14, 468 (1961); (b) M. L. Heffernan, A. J. Jones, and P. J. Black, *Aust. J. Chem.*, **20**, 589 (1967); (c) H. G. Ff. Roberts, *Theor. Chim. Acta*, **15**, 63 (1969); (d) H. G. Ff. Roberts, *ibid.*, **22**, 105 (1971); (e) R. B. Mallion, *J. Mol. Spectrosc.*, **35**, 491 (1970).

(42) (a) More recent work by the Trost group[42b] has extended NMR studies on pyracylene to consider the influence of "ring currents" on ^{13}C chemical shifts.[42c] (b) B. M. Trost and W. B. Herdle, *J. Am. Chem. Soc.*, **98**, 4080 (1976). (c) For some comments by one of the present authors on "ring-current" effects in ^{13}C NMR, see R. B. Mallion, *Nucl. Magn. Reson.*, **4**, 1-66 (1975).

Thermolysis of *n*-Butylsilver(I) Ate Complexes

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Lithium di-*n*-butyl(tri-*n*-butylphosphine)silver(I) (2) and other organosilver(I) ate complexes have been prepared and their mechanism of thermal decomposition studied. Chemical characterization of 2 by reaction first with dibromoethane and then iodine yielded only 1-iodobutane, showing that 2 was formed and that 2 was not in equilibrium with *n*-butyllithium. ^{13}C and ^{31}P NMR spectra of lithium dimethyl(tri-*n*-butylphosphine)silver(I) are described which support this conclusion. Dilithium trimethyl(tri-*n*-butylphosphine)silver(I) was also identified by ^{13}C NMR. Analysis of the products of thermal decomposition of 2 suggests that the observed thermal stabilization of 2 with respect to the rapid thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)silver(I) (1) is the result of an altered mechanism for carbon-silver bond cleavage. Lithium di-*n*-butyl(tri-*n*-butylphosphine)silver(I) is proposed to decompose to give products derived from *n*-butyl radicals and *n*-butyllithium. The principal thermal decomposition products from 2 were octane (26%), butane (71%), and 1-butene (3%). Crossover experiments in which mixed lithium *n*-butyl(*n*-pentyl)silver(I) was thermally decomposed yielded a statistical distribution of coupled products. Substitution of magnesium bromide for lithium had no effect on the product mixture from these thermal decomposition reactions. Kinetics of decomposition of 2 were first order in 2. Other possible pathways for decomposition of organosilver(I) ate complexes are discussed and the suggested mechanism for this thermal decomposition reaction is compared to similar organocopper(I) and organogold(I) chemistry.

The facility with which carbon-metal bond cleavage reactions occur and their mode of scission are a central feature of organometallic chemistry. In the case of organo transition metal compounds, facile thermal cleavage of carbon-metal bonds is often observed and can occur through a variety of mechanistic pathways.[1] Stabilization of organo transition metal compounds with respect to such thermal decomposition has been accomplished by a variety of means.[2,3] Modification of the alkyl ligand of an organo

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(1) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

transition metal compound so as to preclude β-hydride elimination is one example of such a procedure. Addition of extra alkyl ligands to an alkyl transition metal compound to form an ate complex is a second example. However, the origin of the enhanced thermal stability of ate complexes is not well understood. In this paper we report the results of our studies of the mechanism of thermal decomposition of di-*n*-butyl(tri-*n*-butylphosphine)silver(I) (2) ate complexes and contrast our results with the earlier studies in alkyl(tri-*n*-butylphosphine)silver(I),[4] alkyl(tri-*n*-butylphosphine)copper(I),[5] alkylgold(I),[6] and lithium dialkylgold(I)[6] chemistry in an effort to understand the factors involved in these carbon–metal bond cleavage reactions. Our product studies of the thermal decomposition of organosilver(I) ate complexes suggest direct formation of alkyl radicals in thermal decompositions of 2 and thus constitute evidence for a change in the mode of carbon–metal bond scission resulting from ate complex formation.

Organometallic compounds of copper(I), silver(I), and gold(I) have been the subject of many previous studies. Organocopper(I) compounds have received the most attention because of their synthetic importance,[7] but detailed mechanistic research on organogold(I) and -gold(III) reactions has also been published.[6] The thermal decomposition of simple organocopper(I) and organosilver(I) compounds has been thoroughly studied.[4,5,8] Aryl derivatives of each of these metals have also been studied both from a structural and mechanistic point of view.[9] However, aside from Kochi's study of organogold(I) ate complexes, there has been comparatively little work done on the mechanism of thermal decomposition of alkylsilver(I) and alkylcopper(I) ate complexes. The studies reported below have concentrated on lithium dialkyl(tri-*n*-butylphosphine)silver(I) ate complex thermal decompositions because of the contrasts between their thermal decomposition and the known thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)silver(I) (1).

Results and Discussion

Lithium di-*n*-butyl(tri-*n*-butylphosphine)silver(I) can be simply formed by using eq 1 in which 2 equiv of *n*-butyllithium is added to 1 equiv of tetrakis[iodo(tri-*n*-butylphosphine)silver(I)].[10] Initially, 1 formed followed by subsequent conversion of this monoalkyl(tri-*n*-butylphosphine)silver(I) complex into an ate complex. Addition of a 3rd equiv of *n*-butyllithium formed an equilibrium mixture of *n*-butyllithium, 2, and dilithium tri-*n*-butyl(tri-*n*-butylphosphine)silver(I) (vida infra). Evidence for formation of these various complexes comes from several sorts of experiments. First, ^{13}C NMR experiments using methyllithium (50% ^{13}C enriched) for spectral simplicity showed that a 1:1 (equiv/equiv) mixture of methyllithium and tetrakis[iodo(tri-*n*-butylphosphine)silver(I)] quantitatively formed methyl(tri-*n*-butylphosphine)silver(I) as shown by the appearance of a doublet of doublets at δ −8.82 at −80 °C generated by $^{107,109}Ag-^{13}C$ coupling and by the absence of an absorption for methyllithium at δ −12.92.[11] ^{31}P NMR of this compound (no ^{13}C label was used in the ^{31}P NMR experiments) at −80 °C again contained a doublet of doublets characteristic of $^{107,109}Ag-^{31}P$ coupling at δ 5.85 (relative to 85% H_3PO_4).[12] Thus, the phosphine ligand was bound to the silver(I) complex at this temperature. Addition of 2 equiv of methyllithium per 1 equiv of tetrakis[iodo(tri-*n*-butylphosphine)silver(I)] formed a new species which could be detected by ^{13}C NMR as a doublet of doublets at −80 °C at δ −9.90. ^{31}P NMR of this 2:1 complex exhibited a singlet at δ 22.3 and showed no free phosphine, and $^{107,109}Ag-^{31}P$ coupling was not observed as low as −90 °C. On addition of excess phosphine this singlet simply shifted upfield toward the chemical shift of free phosphine. Therefore, fast exchange between free phosphine and the 2:1 complex is probably occurring.[13]

$$2n\text{-}C_4H_9Li + 0.25[IAgP(n\text{-}C_4H_9)_3]_4 \xrightarrow[-78\ ^\circ C]{Et_2O} Li(n\text{-}C_4H_9)_2Ag\cdot P(n\text{-}C_4H_9)_3 + LiI \quad (1)$$

Table I. ^{13}C NMR $^{107,109}Ag-^{13}C$ Coupling Constants for $Li_{n-1}Me_nAg^I$

n	$J_{^{107}Ag-^{13}C}$, Hz	$J_{^{109}Ag-^{13}C}$, Hz
1	130	149
2	85	98
3	66	76
(4)	(~45)	(~51)

Addition of 3 equiv of methyllithium to tetrakis[iodo(tri-*n*-butylphosphine)silver(I)] produced a solution containing three methyl species by ^{13}C NMR. Methyllithium appeared as a broad singlet at δ −12.92. Two other doublets of doublets exhibiting $^{107,109}Ag-^{13}C$ coupling appeared at δ −9.13 and δ −9.92. The complex at δ −9.92 was again assigned to the 2:1 complex while the complex absorbing at δ −9.13 was assigned to the 3:1 methyl–silver(I) complex. Addition of excess methyllithium simply led to an increase in the relative size of the methyllithium and 3:1 complex absorptions. The coupling constants for the three methylsilver species follow a pattern which suggested the complex at δ −9.13 was a 3:1 rather than a 4:1 complex as shown in Table I. A 4:1 complex would have been expected to have a $^{109}Ag-^{13}C$ coupling constant of ca. 51 Hz and a $^{107}Ag-^{13}C$ coupling constant of ca. 45 Hz. The values of $J_{^{107,109}Ag-^{13}C}$ for a hypothetical 4:1 complex were determined by assuming that each successive methyl group which was added to methylsilver decreased the coupling constants by an amount proportional to the ratio of the total number of methyl groups to the previous number of methyl groups on each silver(I) atom. In this fashion $J_{^{109}Ag-^{13}C}$ = 72 Hz and $J_{^{107}Ag-^{13}C}$ = 63 Hz can be calculated for the 3:1 complex in good agreement with experiment.

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[2] A significant number of stable alkyl transition metal compounds are now known; cf.: Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219–41.

[3] Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243–67.

[4] Kendall, P. E.; Bergbreiter, D. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2806–13.

[5] (a) Whitesides, G. M.; Stedronsky, E. R.; Casey, C. P.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 1426–27. (b) Wada, K.; Tamura, M.; Kochi, J. *Ibid.* **1970**, *92*, 6656–8.

[6] Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 8440–6.

[7] Posner, G. H. *Org. React.* **1972**, *19*, 1–113; **1975**, *22*, 253–400. House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59–67.

[8] (a) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379–89. (b) Whitesides, G. M.; Panek, E. J.; Stedronsky, E. R. *Ibid.* **1972**, *94*, 232–9.

[9] van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1979**, *174*, 367–87 and references therein.

[10] For simplicity we have chosen to draw the organometallic compounds in this paper as monomers. We have no evidence on and do not mean to imply anything about possible aggregation on these systems.

[11] ^1H NMR experiments with related alkylcopper(I) ate complexes have been reported; cf.: (a) Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 5312–6; (b) Pearson, R. G.; Gregory, C. D. *Ibid.* **1976**, *98*, 4098–104; (c) San Filippo, J., Jr. *Inorg. Chem.* **1978**, *17*, 275–83.

[12] The coordination of phosphine ligands to silver(I) salts has been described in some detail; cf.: Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386–91.

[13] The apparent coordination of tri-*n*-butylphosphine to 2 is in contrast to the lack of phosphine–gold(I) interaction seen on related lithium dimethylaurate(I) complexes; cf.: (a) Tamaki, A.; Kochi, J. K. *J. Chem. Soc., Dalton Trans.* **1973**, 2620–6; (b) Tobias, R. S.; Rice, G. W. *Inorg. Chem.* **1975**, *14*, 2402–7.

The $\gamma_{^{107}\text{Ag}}/\gamma_{^{109}\text{Ag}}$ was determined to be 0.87 from our data in agreement with literature values.[12] The ^{31}P NMR of this latter reaction mixture which was clearly different from that of the 2:1 complex contained a single absorption down to −90 °C with a chemical shift identical with that of free tri-*n*-butylphosphine (δ 32.76). The chemical shift of this phosphine species did not change on the addition of excess phosphine, confirming its identity. Taken together, these NMR spectra show that discrete 1:1, 2:1, and 3:1 methylsilver(I) complexes form and that the tri-*n*-butylphosphine ligand is associated with the 1:1 complex, is associated at least in an equilibrium sense with the 2:1 complex, and is apparently free in solution when excess methyllithium and the 3:1 complex are present in solution.

We were also able to demonstrate that 2:1 complexes of *n*-butyllithium and silver(I) formed using chemical procedures. Specifically, we examined solutions of **2** prepared according to eq 1 for free *n*-butyllithium. Under conditions in which *n*-butyllithium is known to react quantitatively with excess 1,2-dibromoethane to form 1-bromobutane (−78 °C, ether), no 1-bromobutane (or octane) was observed by gas chromatography upon 1,2-dibromoethane treatment of a −78 °C ethereal solution of **2**. In contrast, a quench of **2** with molecular bromine (or iodine) at −78 °C in ether did show the presence of two butylmetal moieties and 1-bromobutane (or 1-iodobutane) was formed in this case. These results taken together suggest complete formation of **2** according to eq 1. Reaction of 3 equiv of *n*-butyllithium with tetrakis[iodo(tri-*n*-butylphosphine)silver(I)] according to eq 2 was employed to generate **3**. However,

$$3n\text{-C}_4\text{H}_9\text{Li} + 0.25[\text{IAgP}(n\text{-C}_4\text{H}_9)_3]_4 \xrightarrow[-78\ ^\circ\text{C}]{\text{Et}_2\text{O}} \underset{\mathbf{3}}{\text{Li}_2(n\text{-C}_4\text{H}_9)_3\text{Ag}\cdot\text{P}(n\text{-C}_4\text{H}_9)_3} + \text{LiI} \qquad (2)$$

3 formed 1 equiv of 1-bromobutane on treatment with 1,2-dibromoethane at −78 °C in ether and **3** could therefore not be distinguished chemically from a mixture of *n*-butyllithium and **2**. Nevertheless, based on the qualitatively greater thermal stability of ether solutions of **3** ($t_{1/2} \simeq 5$ h at 0 °C) vs. **2** ($t_{1/2} \simeq 2.6$ h at 0 °C), the lesser thermal stability of **3** vs. *n*-butyllithium in ether ($t_{1/2} \simeq 30$ h at 0 °C), and the NMR spectra of related methyl(tri-*n*-butylphosphine)silver(I) ate complexes (vida supra), we believe **3** is formed to some extent.

Warming solutions of **2** to 0 °C with stirring for 48 h led to complete thermal decomposition. This contrasts with the more rapid thermal decomposition of a simple alkylsilver(I) which occurred when solutions of **1** were warmed from −78 to 0 °C.[4] The products of such decomposition reactions are shown in eq 3 and 4. No (*Z*)- or (*E*)-2-butene

$$\mathbf{2} \xrightarrow[48\ \text{h}]{0\ ^\circ\text{C}} \underset{26\%}{n\text{-C}_8\text{H}_{18}} + \underset{71\%}{n\text{-C}_4\text{H}_{10}} + \underset{3\%}{1\text{-C}_4\text{H}_8} \qquad (3)$$

$$\mathbf{1} \xrightarrow{0\ ^\circ\text{C}} \underset{93\%}{n\text{-C}_8\text{H}_{18}} + \underset{5\%}{n\text{-C}_4\text{H}_{10}} + \underset{2\%}{1\text{-C}_4\text{H}_8} \qquad (4)$$

was observed in either case, eliminating the possibility of isomerization of the alkylmetal before decomposition. The low yield of 1-butene also eliminates the possibility of β-hydride elimination as a primary thermal decomposition pathway. The major difference between reactions 3 and 4 is the dramatic decrease in yield for octane formation and the concomitant increase in butane formation observed for decomposition of the ate complex **2**. While the octane product from **1** has been previously explained by a reductive elimination of two butyl groups from a silver cluster, the octane product in reaction 3 can be completely accounted for by the known ratio for disproportionation/combination of *n*-butyl radicals in ether at 30 °C ($k_d/k_c = 0.20 \pm .01$).[4] If we postulate a mechanism like Scheme I, most of the butane product would then arise

Scheme I

$$\mathbf{2} \rightarrow n\text{-C}_4\text{H}_9\cdot + \underset{\mathbf{4}}{(n\text{-C}_4\text{H}_9)\text{AgLi}}$$

$$\mathbf{4} \rightarrow n\text{-C}_4\text{H}_9\text{Li} + \text{Ag}(0)$$

from proton abstraction by *n*-butyllithium from the solvent ether or from protonation of *n*-butyllithium in an aqueous quench. The remainder (21%) of the butane formed in reaction 3 would then arise by hydrogen abstraction from the solvent ether by an *n*-butyl radical. Compounds such as **4** postulated above are without precedent in organosilver chemistry but are not unreasonable as reactive intermediates since other transition metal anions are known.[14]

An alternative mechanism which would still be indicative of *n*-butyl radical intermediates would be dissociation of *n*-butyllithium from **2** at 0 °C to generate an unusually reactive form of **1** (e.g., a monomeric complex). If such a species was very labile, homolytic carbon–silver bond cleavage might then have occurred. Unlike **1** which was postulated to be aggregated in earlier studies of the thermal decomposition of organosilver(I) reagents, a monomeric form of **1** could not decompose by concerted loss of two *n*-butyl groups from an organosilver(I) aggregate. If **2** had first generated *n*-butyllithium and then decomposed to form an *n*-butyl radical by this route, equal amounts of *n*-butyl radicals and *n*-butyllithium would have been produced. A mixture of radical disproportionation, radical combination, hydrogen abstraction, and proton abstraction would then explain the products seen in eq 3 as discussed above. Evidence against this alternative mechanism came from experiments in which **2** was allowed to react with 1,2-dibromoethane while warming to 0 °C. Under these conditions, the product mixture shown in eq

$$\mathbf{2} \xrightarrow[0\ ^\circ\text{C, Et}_2\text{O}]{\text{BrCH}_2\text{CH}_2\text{Br}} \underset{50\%}{1\text{-C}_4\text{H}_9\text{Br}} + \underset{44\%}{n\text{-C}_8\text{H}_{18}} + \underset{6\%}{n\text{-C}_4\text{H}_{10}} + \underset{\text{trace}}{1\text{-C}_4\text{H}_8} \qquad (5)$$

5 was observed. The amounts of the hydrocarbon products in reaction 5 are qualitatively similar to those found for the thermolysis of **1** (eq 3) if we assume that 1-bromobutane was formed first and that the hydrocarbon products then resulted from the thermal decomposition of an unexceptional *n*-butyl(tri-*n*-butylphosphine)silver(I) species. This product mixture is different from the mixture of decomposition products from **2** (eq 3). Taken together these results suggest that **1** was formed in eq 5 and was no different than **1** prepared normally. Thus, these results are not in agreement with a mechanism in which a monomeric or otherwise unusual *n*-butylsilver(I) species was generated as an intermediate in the thermolysis of **2**.

The first step of the proposed mechanism for the thermolysis of **2** is formation of an *n*-butyl radical. In an attempt to detect radical intermediates, ESR spectra were obtained for thermal decompositions of **2** in diethyl ether and in pentane. Samples were taken out of the −78 °C bath and warmed to room temperature while continuously scanning the 2250–4240-G range. No absorptions were observed during decomposition of **2** in either solvent. If alkyl radicals were intermediates they must have been

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(14) (a) Jonas, K.; Pörschke, K. R.; Krüger, C.; Tsay, Y. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 621–2. (b) Dye, J. L. *Ibid.* **1979**, *18*, 587–98. (c) Peer, W.; Laqowski, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 6260–1, 7768–70.

Table II. Solvent and Concentration Effects in Thermal Decomposition of 2

solvent	[2], M	*n*-butane, %	1-butene, %	*n*-octane, %	k_d/k_c
diethyl ether	0.025	87	2	11	0.33
diethyl ether	0.1	71	3	26	0.23
diethyl ether	0.2	62	4	34	0.24
n-pentane	0.1	59	4	37	0.22
tetrahydrofuran	0.1	47	10	43	0.46

present at concentrations below the detection limits of the ESR spectrometer. ^{1}H NMR spectra of thermal decomposition reactions of 2 in ether were also examined but no CIDNP effects were seen. However, the NMR absorptions of solvent limited our ability to detect a CIDNP signal in this experiment.

The second step of the mechanism involves the formation of *n*-butyllithium. To test for this alkyllithium product, an ethereal solution of 2 was partially thermolyzed at 0 °C, then cooled to −78 °C, and quenched with 1,2-dibromoethane followed by iodine. The concentrations of 1-bromobutane detected varied with the extent of partial thermolysis. Since 2 itself was unreactive toward 1,2-dibromoethane at −78 °C (vida supra), the formation of 1-bromobutane under these conditions strongly implicates *n*-butyllithium as a product of the thermolysis of 2.

Experiments in which the nature of the halide ions and the added metal cation have been changed gave results similar to those described by eq 3. Specifically, substitution of bromide for iodide and magnesium for lithium in thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)silver(I) ate complexes had no appreciable affect on product mixtures or on the qualitative rate of these decomposition reactions.

Both the solvent and concentration of the organosilver(I) species affect the relative amounts of octane and butane formed in a thermal decomposition experiment as shown in Table II. Changing the solvent from pentane to diethyl ether results in modest changes in the amount of octane/butane product in accord with expectations based on the relative hydrogen atom donating ability of each solvent. Specifically, less butane (which in Scheme I is proposed to arise partially from abstraction of hydrogen from solvent) was seen in pentane which is a poorer hydrogen-donating solvent than in ether. If octane formation in thermal decomposition of 2 did in fact result from a bimolecular coupling of two butyl radicals as suggested in Scheme I, concentration studies should also yield a modified product ratio. Specifically, low concentrations of 2 should tend to reduce the yield of octane while higher concentrations of 2 should tend to increase the yield of octane. These predictions too are in accord with the results listed in Table II. This simple mechanistic picture does not explain the product mixture seen in THF (less 1-butene and octane were expected).

In Scheme I the initial step is dissociation of 2 to form an alkyl radical and an anionic silver complex. If a lithium dialkyl(tri-*n*-butylphosphine)silver(I) ate complex were formed which contained two different alkyl groups, the initial step might be expected to result in selective formation of the more stable alkyl radical. We have prepared and thermally decomposed the mixed lithium[(*n*-butyl)(methyl)(tri-*n*-butylphosphine)silver(I)] (5) ate complex to test this prediction. A mixed lithium dialkylsilver(I) ate complex was readily prepared according to eq 6. The formation of 5 was verified by quenching solutions of 5 first with dibromoethane at −78 °C and then with iodine (eq 7). The formation of only iodomethane and 1-iodobutane

$$\mathrm{CH_3Li} + n\text{-}\mathrm{C_4H_9Li} + 0.25[\mathrm{IAgP}(n\text{-}\mathrm{C_4H_9})_3]_4 \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} \underset{\mathbf{5}}{\mathrm{Li(CH_3)}(n\text{-}\mathrm{C_4H_9})\mathrm{Ag{\cdot}P}(n\text{-}\mathrm{C_4H_9})_3} \quad (6)$$

$$\mathbf{5} \xrightarrow[2.\ \mathrm{I_2}]{1.\ \mathrm{BrCH_2CH_2Br}} \mathrm{CH_3I} + 1\text{-}\mathrm{C_4H_9I} \quad (7)$$

and no bromomethane or 1-bromobutane established that the starting alkyllithium reagents had been completely converted to organosilver(I) compounds. We did not attempt to distinguish between 5 and other possible dialkyl(tri-*n*-butylphosphine)silver(I) complexes which could be present along with 5 as a result of alkyl-group exchange (e.g., equilibration like that shown in eq 8). Decomposition

$$\underset{\mathbf{2}}{\mathrm{Li}(n\text{-}\mathrm{C_4H_9})_2\mathrm{Ag{\cdot}P}(n\text{-}\mathrm{C_4H_9})_3} + \underset{\mathbf{6}}{\mathrm{Li(CH_3)_2Ag{\cdot}P}(n\text{-}\mathrm{C_4H_9})_3} \rightleftharpoons \underset{\mathbf{5}}{\mathrm{Li(CH_3)}(n\text{-}\mathrm{C_4H_9})\mathrm{Ag{\cdot}P}(n\text{-}\mathrm{C_4H_9})_3} \quad (8)$$

of 5 (or the equilibrium mixture of 2, 5, and 6) produced a mixture of products as shown in eq 9. This thermal

$$\mathbf{5} \xrightarrow[2.\ -78\ ^\circ\mathrm{C},\ \mathrm{I_2}]{1.\ 0\ ^\circ\mathrm{C},\ 96\ \mathrm{h}} \underset{0.90\ \mathrm{mmol}}{\mathrm{CH_3I}} + \underset{0.24\ \mathrm{mmol}}{n\text{-}\mathrm{C_4H_{10}}} + \underset{0.05\ \mathrm{mmol}}{1\text{-}\mathrm{C_4H_8}} + \underset{0.24\ \mathrm{mmol}}{n\text{-}\mathrm{C_5H_{12}}} + \underset{0.18\ \mathrm{mmol}}{n\text{-}\mathrm{C_8H_{18}}} + \underset{\mathrm{none}}{1\text{-}\mathrm{C_4H_9I}} \quad (9)$$

decomposition was quenched with iodine at −78 °C after 96 h to determine how much if any butylmetal or methylmetal species remained. If *n*-butyl radical formation from 2 or 5 was actually more facile than methyl radical formation from 5 or 6 we expected to find a substantial amount of methylmetal species left. The greater yield of iodomethane vs. 1-iodobutane obtained in eq 9 is in accord with our expectations based on the mechanism of Scheme I.

A crossover experiment was performed to test the intermolecularity of the alkyl radical coupling reaction during thermolysis of another mixed lithium (dialkyl)silver(I) ate complex in which two similar but not identical alkyl groups (*n*-butyl and *n*-pentyl) were bound to silver(I). Lithium[(*n*-butyl)(*n*-pentyl)(tri-*n*-butylphosphine)silver(I)] was prepared in the same manner as 5, using *n*-pentyllithium rather than the methyllithium reactant in eq 6. Assuming there would be little or no preference for the formation of *n*-butyl or *n*-pentyl radicals, Scheme I predicts a 1:2:1 ratio of *n*-octane/*n*-nonane/*n*-decane for the thermolysis of lithium[(*n*-butyl)(*n*-pentyl)(tri-*n*-butylphosphine)silver(I)]. Experimentally, the ratio was determined to be 1.0:2.2:0.9 which is in good agreement with our mechanism (eq 10). Thus, mixed dialkylsilver(I) ate

$$\mathrm{Li}(n\text{-}\mathrm{C_4H_9})(n\text{-}\mathrm{C_5H_{11}})\mathrm{Ag{\cdot}P}(n\text{-}\mathrm{C_4H_9})_3 \xrightarrow[0\ ^\circ\mathrm{C},\ 60\ \mathrm{h}]{\mathrm{Et_2O}} n\text{-}\mathrm{C_8H_{18}} + n\text{-}\mathrm{C_9H_{20}} + n\text{-}\mathrm{C_{10}H_{22}} + \text{monomers} \quad (10)$$

complexes give statistical mixtures of products as expected. The preferential decomposition of butyl groups in 5 is therefore due to the different character of a butyl vs. a methyl group rather than to the way 5 was prepared.

The kinetics of decomposition of 2 was also briefly studied. A likely slow step in Scheme I is the first step generating a reactive anionic alkylsilver species and a free radical. If the first step of Scheme I was rate determining, first-order kinetics should be seen. The experimental results shown in Figure 1 show that this is the case. A plot of the natural logarithm of the concentration of unreacted 2 determined as 1-iodobutane (see Experimental Section for details of the kinetic experiments) gave a straight line for four half-lives. The experimentally determined rate constant was 0.27 ± 0.02 h^{-1} with a half-life of 2.6 h. Using

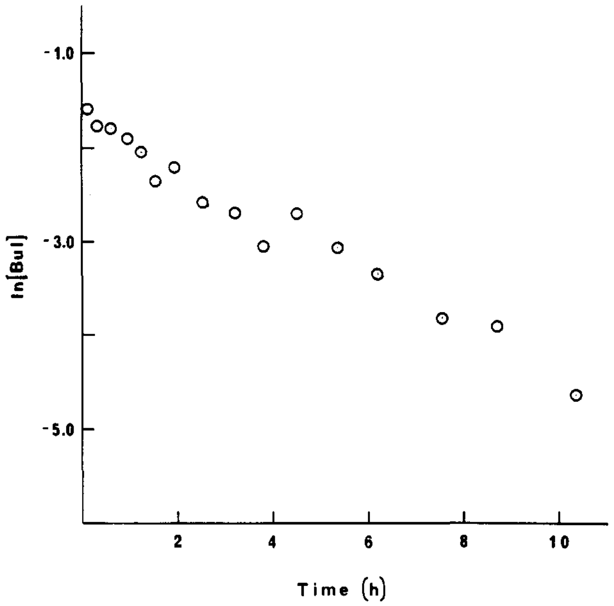
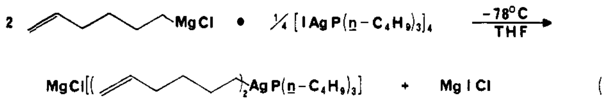


Figure 1. First-order plot of the thermal decomposition of 2 determined by the n-butyl iodide concentration at -4.0 °C.

this rate constant $\Delta G^{\ddagger}$ is calculated to be 21 kcal/mol. Autocatalysis during these decompositions was not seen in contrast to the kinetics of decomposition of other related organometallic species.[1]

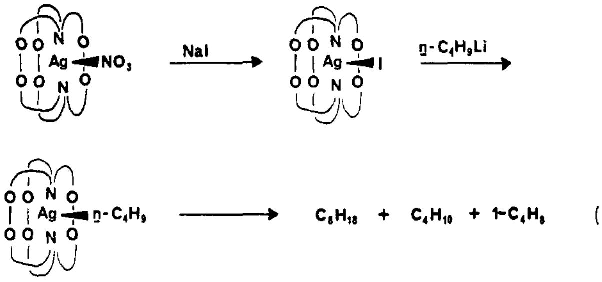
The 5-hexenyl ligand was incorporated into an organosilver(I) ate complex (7) to test for radical formation (eq 11). Cyclization of this 5-hexenyl group to cyclopentylcarbinyl products would indicate a radical intermediate was present if 7 did not isomerize under the reaction conditions.[15] However, cyclization of 7 was found to occur at a rate competitive with thermolysis. Therefore this test could not be used to determine whether intermediate radicals are generated.[16]



(11)

7

Preliminary studies suggest that the other novel complexes of n-butylsilver(I) may also have thermal decomposition pathways unlike those reported for 1. Specifically, the yield of the octane products from decomposition of n-butylsilver(I) complexed with [2.2.2]cryptand (8) (prepared according to eq 12) was substantially lower than that seen in decomposition of 1 (cf. eq 12 and 4). The amounts of product observed in the thermal decomposition of 8 varied from run to run possibly because 8 was formed as a suspension. As a result we cannot speculate on the actual process by which 8 did decompose other than to observe that it was not by a simple β-hydride elimination (too little 1-butene is seen) or by the "concerted" thermal decomposition pathway previously described for 1.



(12)

8

Unlike thermal decomposition of 2 and 1, lithium[di-n-butyl(tri-n-butylphosphine)copper(I)] (9) and n-butyl(tri-n-butylphosphine)copper(I) (10) did not appear to decompose by markedly different mechanisms. The products observed in decomposition of each of these organocopper(I) species are shown in eq 13 and 14.[5a] β-

$$\underset{\mathbf{9}}{\mathrm{Li}(n\text{-}C_4H_9)_2Cu\cdot P(n\text{-}C_4H_9)_3} \rightarrow \underset{65\%}{n\text{-}C_4H_{10}} + \underset{22\%}{1\text{-}C_4H_8} + \underset{9\%}{n\text{-}C_8H_{18}} \quad (13)$$

$$\underset{\mathbf{10}}{(n\text{-}C_4H_9)Cu\cdot P(n\text{-}C_4H_9)_3} \rightarrow \underset{49\%}{n\text{-}C_4H_{10}} + \underset{51\%}{1\text{-}C_4H_8} + \underset{0.3\%}{n\text{-}C_8H_{18}} \quad (14)$$

Hydride elimination appears to be important in the thermal decomposition of 9 based on the relatively high yield of butene. There was a significant amount of n-octane seen so this would appear not to be the only mechanistic pathway for decomposition of these organocopper(I) species. In any case, the thermal decompositions described by eq 13 and 14 are at least similar. Thus, the kinetically observed thermal stabilization of organo transition metal carbon–metal bonds observed on ate complex formation does not necessarily reflect a change in mechanism for carbon–metal bond scission such as we suggest for the case of organosilver(I) reagents.

Conclusion

Several organosilver ate complexes of the general formula lithium[(alkyl)$_2$(tri-n-butylphosphine)silver(I)] have been prepared, characterized, and thermolyzed. ^{31}P and ^{13}C NMR spectra of these ate complexes (alkyl = methyl) confirmed the formation of soluble complexes with alkyl/silver(I) ratios of 1:1, 2:1, and 3:1. The 3:1 complex consisted of an equilibrium mixture including both the 2:1 complex and alkyllithium reagent. The phosphine was bound to the 1:1 complex at -80 °C but facile phosphine ligand exchange with free phosphine apparently occurred for the 2:1 complex. The phosphine was apparently free in solution when excess methyllithium was present.

The complex 2 was found to be more thermally stable than 1 and produced n-octane (26%), n-butane (71%), and 1-butene (3%) upon thermal decomposition in sharp contrast to the thermolysis products of 1 (eq 4). These differences between 1 and 2 are ascribed to a change in the mode of decomposition resulting from ate complex formation. The mechanism suggested for thermolysis of 2 is initial generation of a primary n-butyl radical followed by elimination of n-butyllithium from an intermediate anionic silver(0) complex (Scheme I). Several data support this mechanism. First, the low yield of octane precludes an alkyl-coupling pathway as being the predominant mode of decomposition. Second, the low yield of 1-butene suggests a β-hydride elimination cannot be an important pathway for decomposition. Third, the ratio of 1-butene to n-octane yields a $k_d/k_c = 0.23$ at 0 °C which is comparable to the known k_d/k_c for n-butyl radicals in ether. Fourth, thermolysis of 2 in the presence of 1,2-dibromoethane results in a high n-octane yield (44%), suggesting 1 is not an intermediate in decomposition of 2. Fifth,

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(15) Ingold, K. U. In "Organic Free Radicals"; Pryor, W. A., Ed.; American Chemical Society: Washington, D.C. 1978; pp 187–207. Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355–7.

(16) Facile cyclization of 5-hexenyl groups bound to transition metals has been reported previously both in the case of silver(I) (ref 4) and zirconium (ref 17).

(17) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3321–31.

changes in the hydrogen-donating ability of the solvent or concentration affect the product distribution in a reasonably predictable fashion. Sixth, when the mixed lithium[(*n*-butyl)(methyl)(tri-*n*-butylphosphine)silver(I)] (**5**) ate complex was thermolyzed, a large percentage of CH_3Li was formed in accord with the expectation that the more stable butyl radical would preferentially be formed. Seventh, the thermolysis of lithium[(*n*-butyl)(*n*-pentyl)(tri-*n*-butylphosphine)silver(I)] yielded a statistical 1.0:2.2:0.9 ratio of *n*-octane/*n*-nonane/*n*-decane, supporting the suggestion that the coupled product, *n*-octane, in **5** thermolysis results from the intermolecular combination of *n*-butyl radicals rather than from the fact that **5** is a "mixed" dialkylsilver(I) species. Finally, first-order kinetics were observed for thermolysis of **2** consistent with the mechanism in Scheme I.

The change in decomposition mechanism observed after ate complex formation in these *n*-butylsilver(I) compounds may reflect a rather subtle difference in activation energy for different pathways for thermal decomposition of carbon–silver bonds.[4,8,18] Free-radical intermediates have already been implicated in previous studies of the thermal decomposition of alkylsilver(I) compounds.[8b] Weakening of the carbon–silver(I) bond from the addition of an extra alkyl ligand which would facilitate homolysis may also be a factor, as has been suggested for dimethylnickel.[19,20]

Organocopper(I) ate complexes such as **9** are qualitatively more thermally stable than **10**. However, these two different organocopper(I) compounds do not thermally decompose by markedly different mechanisms. β-Hydride elimination has been shown to be responsible for the decomposition of **10** and appears also to be important in the decomposition of **9** since 22% 1-butene was produced (eq 13). Thus, thermal stability need not reflect a change in decomposition mechanism as found in organosilver complexes.

Experimental Section

All reactions were carried out in flame-dried glassware under prepurified N_2. Pentane and ethereal solvents were distilled from suspensions of sodium benzophenone dianion. The normality of *n*-butyllithium in hexane (Aldrich), methyllithium in diethyl ether (Aldrich), and *n*-pentyllithium was determined by titration of a 1-mL aliquot under a nitrogen atmosphere with a 0.94 N *sec*-butyl alcohol in xylene solution, using 1,10-phenanthroline as an indicator. *n*-Butylmagnesium bromide was titrated with the same *sec*-butyl alcohol solution, using 2,2′-bipyridine as the indicator. ^{13}C and ^{31}P NMR experiments were performed on a Varian XL-200 spectrometer and a JEOL PFT-100 spectrometer, respectively. NMR samples were prepared in 10-mm o.d. NMR tubes which were fitted with septa and flushed with nitrogen. Benzene-d_6 was used for the internal lock. ^{13}C NMR chemical shifts were reported with respect to Me_4Si as determined from benzene-d_6, assuming a chemical shift of δ 128.0 for benzene. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. A Varian E-6S spectrometer was used for ESR analysis with samples prepared in the same manner as the NMR studies excluding benzene-d_6. All analytical GLC analyses were performed on a Hewlett-Packard 5830A gas chromatograph. Absolute yields of hydrocarbon products were measured by the internal standard method and response factors were determined by using authentic materials. C_4 hydrocarbons and *n*-pentane were analyzed on a 10 ft × $^1/_8$ in. *n*-octane/Porasil C column at 45 °C. Higher molecular weight hydrocarbons and alkyl halides were analyzed on a 6 ft × $^1/_8$ in. UCW-98 column at 75 °C or a 12 ft × $^1/_8$ in. polyphenyl ether (6 ring) column programmed between 70 and 120 °C. All product yields were corrected for residual hydrocarbons in starting materials. Tetrakis[iodo(tri-*n*-butylphosphine)silver(I)] was prepared by the procedure of Mann, Purdie, and Wells[21] in 60% yield and had mp 42–43 °C (lit.[21] mp 43 °C).

***n*-Butyl(tri-*n*-butylphosphine)silver(I) (1)** was prepared as previously described[4] as a clear and colorless solution that was used directly for further reactions.

Lithio[di-*n*-butyl(tri-*n*-butylphosphine)silver(I)] (2) and **dilithio[tri-*n*-butyl(tri-*n*-butylphosphine)silver(I)] (3)** were prepared by using a procedure similar to that used for **1** with the exception that 2 mequiv (1.35 mL of 1.48 N), and 3 mequiv (2.03 mL of 1.48 N), respectively, of *n*-butyllithium were added to a cold diethyl ether solution of 1 mequiv of tetrakis[iodo(tri-*n*-butylphosphine)silver(I)].

Methyl(tri-*n*-butylphosphine)silver(I) species used in NMR studies were prepared as ether solutions in the same manner as their corresponding *n*-butylsilver ate complexes by substituting methyllithium for *n*-butyllithium. The 50% ^{13}C-enriched methyllithium for ^{13}C NMR studies was prepared from 90% ^{13}C-enriched methyl iodide (KOR Inc.) and *n*-butyllithium by following a method by McKeever et al.[22]

Chemical Characterization of 1–3 with Dibromoethane. Solutions of **1**–**3** were prepared as previously described with internal standards for GC analysis. An excess of dibromoethane was introduced into the solutions (at −78 °C) followed by 0.5 mL of 10% HCl 10 min later. No 1-bromobutane was formed from solutions of either **1** or **2** while 1 equiv of 1-bromobutane was produced from **3**.

Bromomagnesium[di-*n*-butyl(tri-*n*-butylphosphine)silver(I)] was prepared by the addition of 2 mequiv of *n*-butylmagnesium bromide to 1 mequiv of tetrakis[iodo(tri-*n*-butylphosphine)silver(I)] in diethyl ether at −78 °C to yield a 0.1 N solution.

The thermal decompositions of the organosilver and -copper ate complexes were performed by adding *n*-nonane and *n*-pentane as the internal standards, warming to 0 °C or room temperature, and quenching at the appropriate time with H_2O, 1,2-dibromoethane, or I_2. **2** was also thermolyzed in the presence of 1,2-dibromoethane by injecting an excess of the dihalide into a solution of **2** at −78 °C and warming to 0 °C (cf. eq 5).

Lithium[(*n*-butyl)(methyl)(tri-*n*-butylphosphine)silver(I)] (5) was prepared by the addition of 1 equiv of CH_3Li to 1 equiv of **1**. This mixed dialkylsilver(I) species was characterized by first adding an excess of 1,2-dibromoethane to a −78 °C solution of **5**, followed by an excess of I_2 in ether 10 min later. Only iodomethane and 1-iodobutane were formed as determined by GLC. A solution of **5** was thermolyzed by warming to 0 °C for ca. 96 h, cooling to −78 °C, and quenching with an ethereal I_2 solution. Products were analyzed by GLC, using *n*-heptane as the internal standard.

Lithium[(*n*-butyl)(*n*-pentyl)(tri-*n*-butylphosphine)silver(I)]. An ether solution of *n*-pentyllithium was prepared as previously described for *n*-butyllithium from *n*-pentyl bromide and lithium wire.[23] *n*-Pentyllithium (1 mequiv) was then added to the −78 °C ether solution of **1**, thermolyzed at 0 °C for 60 h and analyzed for *n*-octane, *n*-nonane, and *n*-decane.

Kinetics of Thermolyses of 2. Aliquots were removed through a cannula from a 0.1 N 40-mL solution of **2**, cooled to −78 °C, quenched first with 1,2-dibromoethane and then with I_2. Since the 1,2-dibromoethane reacted with *n*-butyllithium at −78 °C but not with the organosilver species and I_2 reacted with any remaining organosilver, forming 1-iodobutane, the amount of **2** present was equal to half of the amount of iodobutane present. The best straight line was obtained from a first-order plot of ln [1-C_4H_9I] vs. time, giving a correlation coefficient of −0.986 and a $t_{1/2}$ of 2.6 h.

Chloromagnesium[di-5-hexenyl(tri-*n*-butylphosphine)silver(I)] (7) was prepared by the addition of 2 equiv of 5-

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(18) (a) Tamura, M.; Kochi, J. K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1120–7. (b) Brown, H. C.; Synder, C. H. *J. Am. Chem. Soc.* **1961**, *83*, 1002–3. (c) Yamamoto, K.; Nakanishi, K.; Kumada, K. *J. Organomet. Chem.* **1967**, *7*, 197–202.

(19) Akermark, B.; Johansen, H.; Roos, B.; Wahlgren, U. *J. Am. Chem. Soc.* **1979**, *101*, 5876–83.

(20) The presence or absence of extra ligands profoundly affects the mechanism of decomposition of nickel(II) metallocycles; cf.: Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. *J. Am. Chem. Soc.* **1978**, *100*, 2418–25.

(21) Mann, F. G.; Wells, A. F.; Purdie, D. *J. Chem. Soc.* **1937**, 1828–36.

(22) McKeever, L. D.; Waack, R.; Doran, M. A.; Baker, E. B. *J. Am. Chem. Soc.* **1969**, *91*, 1057–61.

(23) Jones, R. G.; Gilman, H. *Org. React.* **1951**, *6*, 339–66.

hexenylmagnesium chloride to 1 equiv of tetrakis[bromo(tri-*n*-butylphosphine)silver(I)][4] in THF at −78 °C. This solution of **7** was warmed to 0 °C for 45 min, cooled to −78 °C, and quenched with a THF solution of I_2. Cyclization of the 5-hexenyl group bound to silver was found to increase from 11% to 48% as detected by GLC analysis of 1-iodo-5-hexene and cyclopentylmethyl iodide.

[Ag(2.2.2)]I. [Ag(2.2.2)]NO_3 (0.546 g, 1.00 mmol), which was prepared by following a procedure reported by Lehn[24] in 88% yield, mp 200 °C (lit.[24] mp 200 °C), was dissolved in 70 mL of dry ethanol under N_2. Sodium iodide (0.150 g, 1.00 mmol) was dissolved in 10 mL of dry ethanol and added by syringe to the stirred cryptate solution, precipitating $NaNO_3$ immediately. The mixture was filtered, the solvent was removed on a rotary evaporator and the solid residue was dried under vacuum (1 torr, 24 h). A 74% yield was realized: mp 245–249 °C dec; ^1H NMR ($CDCl_3$) δ 2.70 (t, 12, J = 6 Hz), 3.69 (br s, 24).

***n*-Butyl[Ag(2.2.2)] (8).** [Ag(2.2.2)]I (0.0918 g, 0.150 mmol) was mixed with THF (5 mL) in a N_2-flushed centrifuge tube. The cryptate did not dissolve. The resulting suspension was then cooled to −78 °C for 0.5 h at which point 1 mequiv of *n*-butyllithium was added. The original suspension did not dissolve and thermal decompositions consequently had to be carried out by using the resulting suspension.

Tetrakis[iodo(tri-*n*-butylphosphine)]copper(I) was synthesized by the method previously described[25] in 66% yield, mp 72 °C (lit.[25] mp 75 °C).

***n*-Butyl(tri-*n*-butylphosphine)copper(I) (10)** was synthesized as previously described[5a] and **lithio(di-*n*-butyl)(tri-*n*-butylphosphine)copper(I) (9)** was prepared by treating **10** with an additional 1 equiv of *n*-butyllithium.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for generous support of this work. Funds for the Varian XL-200 NMR spectrometer used in this work were provided, in part, by National Science Foundation grants to Texas A&M University (CHE78-03230). We thank Ms. J. Pusel for experimental assistance in preparing **8** and its precursors.

Registry No. **1**, 52543-55-2; **2**, 76011-13-7; **3**, 76011-14-8; **5**, 76010-99-6; **7**, 76011-01-3; **8**, 76095-41-5; **9**, 24743-93-9; **10**, 26679-41-4; tetrakis[iodo(tri-*n*-butylphosphine)silver(I)], 59448-71-4; 1-bromobutane, 109-65-9; bromomagnesium[di-*n*-butyl(tri-*n*-butylphosphine)silver(I)], 76011-03-5; lithium[(*n*-butyl)(*n*-pentyl)(tri-*n*-butylphosphine)silver(I)], 76011-04-6; 5-hexenylmagnesium chloride, 52669-93-9; butylmagnesium bromide, 693-03-8; tetrakis[bromo(tri-*n*-butylphosphine)silver(I)], 76011-05-7; [Ag(2.2.2)]I, 76095-42-6; tetrakis[iodo(tri-*n*-butylphosphine)copper(I)], 59245-99-7; methylsilver, 75993-65-6; lithium[dimethylsilver(I)], 76011-10-4; dilithium[trimethylsilver(I)], 76011-11-5; trilithium[tetramethylsilver(I)], 76011-12-6; butane, 106-97-8; 1-butene, 106-98-9; octane, 111-65-9; methyl iodide, 74-88-4; pentane, 109-66-0.

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[24] Dietrich, B.; Lehn, J. M.; Sauvage, J. P. *Tetrahedron* **1973**, *29*, 1647–58.

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Electrophilic Attack of Elemental Fluorine on Organic Halogens. Synthesis of Fluoroadamantanes

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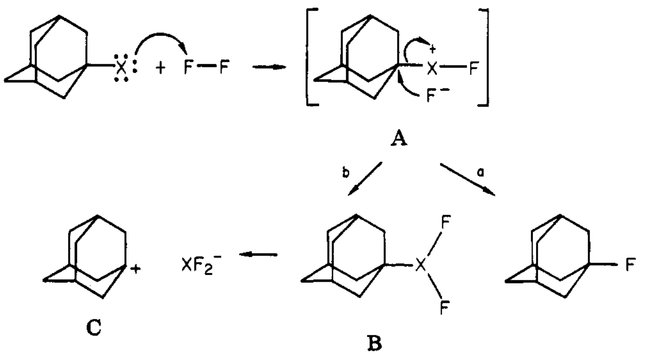
Elemental fluorine acts on bromo- and iodoadamantanes in an electrophilic mode to produce the corresponding fluoroadamantanes. The course of the reaction was investigated in several solvents. It was found that the best yields of the fluoroadamantanes were obtained when Freon ($CFCl_3$) or Freon–chloroform was used. Using methylene chloride as a solvent with iodoadamantanes—but not with the bromo derivatives—resulted in considerable amounts of the corresponding chloro compounds.

Nucleophilic substitution by halogen anion on a carbon bonded to another halogen is a well-established and known procedure. As a matter of fact, a large part of the "classic" fluorine chemistry deals with such nucleophilic substitutions.[1] There are, however, very few examples of replacement of halogen by another halogen atom at a saturated center in which an electrophilic attack is involved. Most of this work concentrates on exchange of iodine with organic iodides.[2] Other examples which do not deal with replacement of the halogen but rather with oxidations due to electrophilic attack of IF_5[3] or its "tamed" aromatic analogue[4] on organic iodides and bromides are also known, but again such examples are limited.

Scheme I



We describe here the reaction of elemental fluorine with some bromo- and iodoadamantanes at −70 °C in various solvents. The results of these experiments are summarized

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[1] See, for example: Chambers, R. D. "Fluorine in Organic Chemistry"; John Wiley and Sons: New York, 1973; Chapters 2 and 3.

[2] de la Mare, P. B. D.; Swedlund, B. E. In "The Chemistry of Functional Groups"; Patai, S., Ed.; Wiley: New York, 1973; Part 1, Chapter 7, p407.

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[10] Tabushi, I.; Aoyama, Y. *J. Org. Chem.* **1973**, *38*, 3447.