bond can clearly be seen, although the interaction between the two is still strong. The large backside lobe on C_1 and the strong resemblance to an unsymmetrical π system are indicative of polar bonding, but the extension of electron density to the metal (the antibonding lobe at Mg is due to core orbitals) is clearly more significant than in **5**-Li.

Conclusions

Allyllithium and allylsodium monomers prefer symmetrically bridged C_s structures. Allylmagnesium hydride monomer has a C_1 structure that represents a compromise between the bridged and "classical" geometries.

The barrier of rotation in *monomeric* allylsodium should be lower than that in *monomeric* allyllithium. The 1,3 MgH shift barrier in allylmagnesium hydride is calculated to be lower than the barrier to rotation. Both are rather small.

The geometry of the C_3H_5 fragment in C_3H_5M shows increasingly large deviations in the order M = Na < Li < MgH from the allyl anion geometry. We attribute the observation of the same, reduced C_2–H coupling constants to the compensating effects of CCC angle widening (greatest in the allyl anion and with the heavier metal counterions) and C_2–H out-of-plane bending (greatest for lithium). These effects should also be present in the π-allyl complexes of transition metals.[8,21]

The direction of electron density toward the metal is achieved largely by twisting pure p orbitals on carbon, although the HOMO of allyllithium shows about 25% s character on C_1 and C_3. Carbon–metal bonds are largely electrostatic in nature, but multicenter covalent bonding nonetheless contributes between 4 and 12 kcal/mol to the stability of allyllithiums. The role of the metal can be represented as a point charge with an ionic radius due to the core orbitals. Many of the differences observed between lithium and sodium are therefore simple distance effects.

Acknowledgment. We are particularly grateful to Prof. A. Streitwieser, Jr., for stimulating discussions on the nature of C–Li bonding and for preprints of relevant work. Thanks are due to Prof. E. Weiss and Dr. C. Krueger for making unpublished X-ray structures available to us and to Prof. W. J. Hehre for allowing us to use basis sets before publication. This work was supported by the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. The cooperation of the Regionales Rechenzentrum Erlangen is gratefully acknowledged.

Note Added in Proof. Decher and Boche's[43] MNDO examination of allyllithium and solvated models (with two and three attached water molecules) has led to the same conclusions regarding the out-of-plane bending of the hydrogens. They also attribute the abnormal C_2–H coupling constants[19] primarily to CCC angle bending and call attention to the related X-ray structure of dilithiohexatriene–bis(tetramethylethylenediamine)[44] in which the "inner" hydrogens, as in allyllithium, are bent most strongly out of the plane of the carbon atoms.

Registry No. C_3H_5Li, 3052-45-7; C_3H_5Na, 2521-40-6; C_3H_5MgH, 86584-37-4.

Supplementary Material Available: Listings of 3-21G optimized geometries for allyllithium, -sodium, and -magnesium hydride isomers (4 pages). Ordering information is given on any current masterhead page.

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Interaction of Alkali Metals with Unsaturated Heterocyclic Compounds. The Reductive Metalation of 3-Phenylcinnoline

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Received March 17, 1983

The reductive metalation of the cinnoline ring system was explored by using 3-phenylcinnoline, **1**. A dianion, **2**, formed with sodium and tetrahydrofuran, showed preferential reactivity at the 1,4-positions with various reagents. After initial reaction at the 4-position, the residual-delocalized 1-anion was a weak nucleophile and reacted only under favorable conditions.

The reductive metalation of conjugated unsaturated systems containing nitrogen has been studied for some time.[1,2] Several such conjugated systems are more readily available in heterocyclic compounds than in open-chain analogues. In addition, the reductive metalation of heterocyclic systems can provide synthetically useful dihydro dianionic derivatives. In this report, the reductive metalation of the cinnoline ring is described, using 3-phenylcinnoline as the example. Here, the reduction of conjugated alkene and azo functionalities is examined for the first time.

Reduction of 3-phenylcinnoline, **1**, with sodium in tetrahydrofuran (THF) occurred rapidly to form dianion **2**. The chemical behavior of **2** toward several reagents was

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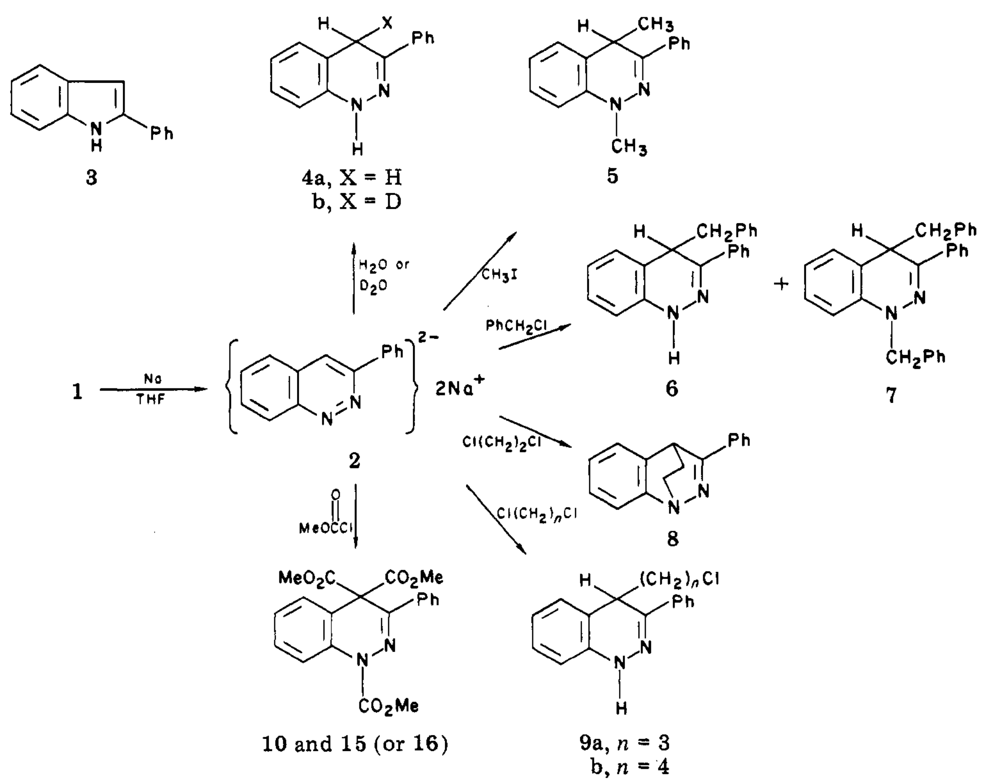
Scheme I. Reactions of the 3-Phenylcinnoline Dianion



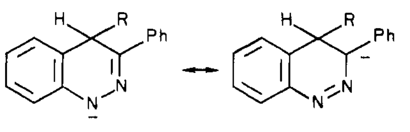
examined. Protonation of **2** generated chiefly 1,4-dihydro-3-phenylcinnoline, **4a**. This compound is known to be formed with a variety of reducing reagents under both acidic and basic conditions.[3] With deuterium oxide, under the present reaction conditions, 4-deuterio-1,4-dihydro-3-phenyl-cinnoline, **4b**, was formed.

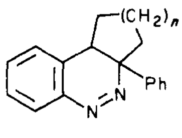
A coproduct detected in these reductive metalations in low yields was 2-phenylindole, **3**. The transformation of **4a** to **3** under acidic conditions has been well documented,[3] and, indeed, reduction of substituted cinnolines with sodium and ethanol produced substituted indoles as coreduction products.[4] Since the indole **3** was detected in all the reductive metalations examined here, it must be a coreduction product even under the aprotic conditions utilized in the present study.

Alkylation of dianion **2** with either methyl iodide or benzyl chloride produced the 1,4-dialkyl-1,4-dihydro-3-phenylcinnolines, **5** and **7**, respectively. These must be kinetic products since alkyl group rearrangement from the 3- to the 1-position is highly unlikely under the conditions used. By analogy, **4** is also a kinetic product and isomerization of an initially formed 1,2-dihydrocinnoline is not occurring.

Since the anionic centers of dianion **2** are highly delocalized, attempts were made to direct reactions to the 3,4-positions by using 1,3-dichloropropane and 1,4-dichlorobutane as alkylating agents. The chloroalkanes were selected to avoid the problems of electron transfer associated with bromo- and iodoalkanes.[7]

Surprisingly, only the monoalkylation products **9a,b** were isolated. Obviously, the monoalkylated monoanion **11** must be a relatively weak nucleophile since subsequent alkylation to **12** was not observed. Indeed, even with benzyl chloride, significant amounts of the monoalkylated derivative **6** was isolated.


11


12, *n* = 1, 2

In contrast to these observations, dianion **2** reacted with 1,2-dichloroethane to produce the bridged product 1,4-ethano-1,4-dihydro-3-phenylcinnoline, **8**. While initial alkylation with these three dichloroalkanes must have occurred at the 4-position, the chlorodimethylene substituent so formed exhibited a greater reactivity toward the remaining anionic site than did the other two chloropolymethylene substituents.

Examination of molecular models showed an interesting difference between the second alkylation step involving the chlorodimethylene vs. the chlorotrimethylene (or chlorotetramethylene) substituents. With the assumption that the alkylation proceeded at the 1-position by nucleophilic substitution, the leaving group (chloride) must adopt a staggered conformation relative to the attached methylene group in the case of the chlorodimethylene substituent forming **8**. In contrast, an eclipsed conformation was required between the leaving group and its adjacent methylene group when the attached chain was three or four carbon atoms long. It is suggested that this conformational distinction provides sufficient difference in activation energy that dialkylation is successful only with 1,2-dichloroethane.

Reaction of 1,4-dihydrocinnolines with esters[5] and anhydrides[6] occurs preferentially at the nitrogens to form

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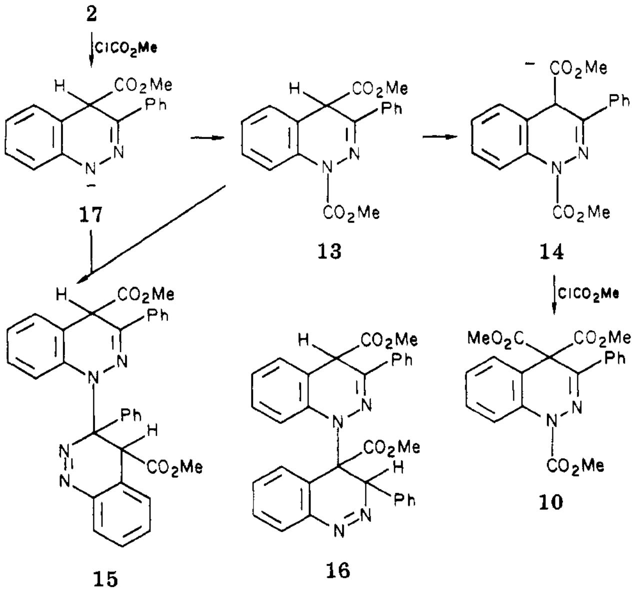
Scheme II. Acylation of the 3-Phenylcinnoline Dianion



derivatives of 1,2-dihydrocinnolines. Since selective reaction at nitrogen by ethyl chloroformate had been observed[8] in the case of the benzophenone anil dianion, the analogous reaction with **2** was examined.

Once again, reaction at the 1,4-positions was observed but the reaction was complicated by proton transfer and the main isolated product was 1,4,4-tricarbomethoxy-1,4-dihydro-3-phenylcinnoline, **10**. Obviously, diacylation occurred producing **13** (Scheme II) which, under the basic conditions of the reaction, lost the labile α-(4)-H forming **14** and ultimately **10**. Accompanying **10** was a dicarbomethoxy dimeric product whose NMR spectrum showed two carbomethoxy groups with very similar chemical shifts as well as two isolated protons also with similar shifts. These spectral characteristics indicated an unsymmetrical dimer, and, since no NH group was present, structures **15** and **16** are possibilities.

While it is not possible to distinguish between these two structures at this point, **15** is favored. First, the chemical shifts of the carbomethoxy groups and the nonaromatic protons in **15** should be more in agreement with those observed than in the case of **16**. Second, it is possible to rationalize the formation of **15** by means of a nucleophilic addition of the monoacylated monoanion **17** to **13** with loss of an *N*-carbomethoxy group.[14]

Experimental Section

Melting points were determined in open capillaries with a Mel-Temp apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Beckman Acculab 10 spectrometer, and NMR spectra were determined on a Bruker WP-80 spectrometer with tetramethylsilane (Me_4Si) as an internal standard. Mass spectra were obtained with a VG 7070F mass spectrometer. Chemical analyses were determined by MHW Laboratories, Phoenix, AZ.

Column chromatography was performed with Silica Gel 60 particle size, 0.063–0.200 mm purchased from E. Merck AG. Thin-layer chromatography (TLC) was effected with Eastman Kodak Chromagram 13181 silica gel sheets.

3-Phenylcinnoline (mp 120–120.5 °C) was prepared by a published procedure[9] and its properties agreed with those already described.[10] Tetrahydrofuran (THF) was dried by distillation from lithium aluminum hydride ($LiAlH_4$) under nitrogen, stored over $LiAlH_4$, and redistilled immediately before use.

The formation of the dianion of 3-phenylcinnoline, **2**, was studied by shaking 1 g (4.85 mmol) of **1** with excess sodium (*ca.* 1 g) and 100 mL of THF in an argon-filled Schlenk tube by means of procedures described previously.[11] Formation of the deep red **2** was rapid, and a reaction time of 8–12 h was adequate for complete reaction.

Preparation of 1,4-Dimethyl-3-phenyl-1,4-dihydrocinnoline, 5. General Procedure. Dianion **2** was generated from 1.0 g (4.85 mmol) of **1** in 100 mL of THF by using 1 g (0.04 mol) of sodium. A specially designed flask[12] that enabled the excess metallic sodium to be removed from the final solution of **2** was used. After 12 h of reaction, the excess sodium was removed from the solution of **2** and the deep red solution was cooled in dry ice–2-propanol. Methyl iodide (0.78 mL, 12.5 mmol) was injected into the stirred reaction mixture through the septum-capped side arm. Stirring was continued at −78 °C for 4 h, and then the reaction mixture was allowed to warm to room temperature.

The final pale yellow solution was diluted with water and extracted with diethyl ether. The ether solution was dried ($MgSO_4$) and evaporated. Thin-layer chromatography (TLC) was performed at this point to evaluate subsequent isolation procedures, and 2-phenylindole was detected (both here and in the other reaction products). The crude reaction product was chromatographed on silica gel with benzene as eluant. The product **5** eluted first: 0.765 g (67%); a pale yellow solid; mp 80–85 °C.

The analytical sample was obtained by recrystallization from 30–60 °C petroleum ether: mp 87–88 °C; IR (KBr) 1600, 1560, 1490, 1440, 1290, 1200, 930, 750 cm^{-1}; NMR ($CDCl_3$) δ 1.19 (d, 3 H, J = 7 Hz), 3.56 (s, 3 H), 4.22 (q, 1 H, J = 7 Hz), 6.8–7.5 (m, 7 H), 7.8–8.0 (m, 2 H); MS, *m/e* (relative intensity) 236 (13, M^+), 222 (17), 221 (100). Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.31; H, 6.83; N, 11.85. Found: C, 81.34; H, 6.84; N, 11.99.

Attempts to characterize the material remaining on the column were not successful.

Preparation of 1,4-Dihydro-3-phenylcinnoline, 4a. The crude reaction product produced by treatment of 4.85 mmol of dianion **2** with 1 mL of water was chromatographed on silica gel with benzene as eluant. The first material to elute was 2-phenylindole (0.101 g, 11%).[13] This was followed by 0.758 g (75%) of **4a**, mp 152–154 °C.

The remaining material, removed from the column with benzene–5% methanol, proved to be starting material, **1** (0.14 g, 14% recovery).[13]

Recrystallization from heptane provided the analytical sample of **4a**: mp 152–153 °C (lit.[9] 152–153 °C); IR (KBr) 3400, 1590, 1480, 1360, 1310, 750, 690 cm^{-1}; NMR (acetone-d_6) δ 3.81 (s, 2 H), 6.8–7.5 (m, 7 H), 7.8–8.1 (m, 2 H), 9.25 (br s, 1 H, exchanges with D_2O); MS, *m/e* (relative intensity) 208 (88, M^+), 207 (100), 131 (24), 104 (23).

Preparation of 4-Deuterio-1,4-dihydro-3-phenylcinnoline, 4b. The previous experiment was repeated by using deuterium oxide in place of the water. The crude reaction product (0.94 g, mp 147–148 °C) was chromatographed as previously described, and 43 mg (5%) of 2-phenylindole followed by 0.72 g of **4b** (71%, mp 153–155 °C) was collected.

Recrystallization from ethanol provided a purified sample: mp 154–155 °C; IR (KBr) 3400, 2960, 1580, 1480, 750 cm^{-1}; NMR (acetone-d_6) δ 3.8 (br s, 1 H, sharpens with D_2O), 6.8–7.5 (m, 7 H), 7.7–8.0 (m, 2 H), 9.2 (br s, 1 H, exchanges with D_2O); MS, *m/e* (relative intensity) 209 (95), 208 (100), 207 (76), 179 (22), 178 (19), 132 (27).

Preparation of 4-Benzyl- and 1,4-Dibenzyl-1,4-dihydro-3-phenylcinnolines, 6 and 7. Dianion **2**, derived from 1.03 g (5 mmol) of **1**, was treated as usual with 1.44 mL (12.5 mmol) of benzyl chloride. The crude reaction product (2.01 g) was chromatographed on silica gel with toluene as eluant. The early

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[11] See ref 7a and references cited therein.

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[13] Identified by comparison of the melting point and IR and NMR spectra with those of authentic material. Thin-layer chromatography of the crude reaction products in this case and in the others demonstrated that 2-phenylindole was present.

[14] A similar elimination has been observed earlier: MacPherson, E. J.; Smith, J. G. *J. Org. Chem.* **1971**, *36*, 2516.

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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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

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