Reactions of Cyclometalated Palladium Complexes with Organolithium Compounds or Grignard Reagents. Selective Ortho Alkylation and Arylation of Benzaldehydes, Azobenzenes, and Tertiary Benzylic Amines

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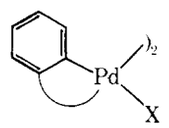
Cyclometalated complexes, di-μ-chloro-bis[2-(phenylazo)phenyl]dipalladium (**2**), di-μ-chloro-bis[2-(*N*,*N*-dimethylaminomethyl)phenyl]dipalladium (**3**), and di-μ-chloro-bis[2-(*N*-phenylformimidolyl)phenyl]dipalladium (**4**), can undergo coupling reactions with either organolithium compounds or Grignard reagents in the presence of triphenylphosphine, giving the corresponding ortho-substituted aromatic compounds highly efficiently. 2-Substituted complexes of **4** (**11–13**) were prepared from the corresponding 2-substituted benzaldehyde in over 94% yield. Similar methylation reactions of **11–13**, followed by hydrolysis, gave 2,6-disubstituted benzaldehydes **15**, **21**, and **22** in high yields. Secondary alkyllithium compounds undergo the cross-coupling reaction accompanied by alkyl group isomerization from secondary to primary. The products are assumed to be formed via a nucleophilic attack of the carbon nucleophile on the phosphine-coordinated palladium monomer of **1**, giving arylalkylpalladium intermediates, which form products by reductive coupling.

Numerous compounds containing a transition metal σ bonded to an aromatic ring derived by cyclometalation have been reported in recent years. These compounds encompass a variety of transition metals and also different types of substitution on the benzene ring.[1-4] Structural studies of the complexes have received widespread attention.[1-5] On the other hand, few studies have been carried out aiming at using these complexes for organic synthesis. Ortho deuteriation can be performed by reductive cleavage of metalated compounds with $LiAlD_4$[6] or the specific ortho hydrogen/deuterium exchange on treatment of complexes such as $RhCl[P(OPh_3)]_3$ or $RuHCl(PPh_3)_3$ with D_2.[4,7] The ortho positions of azobenzene are chlorinated upon reaction with chlorine in the presence of catalytic quantities of $PdCl_2$.[8] Carbonylation[9-12] or reaction with isocyanides[13] of ortho palladation products from α-arylnitrogen derivatives and palladium salts provides a convenient process for synthesis of various heterocyclic compounds. Cyclopalladation complexes react with α olefins,[14] acrylic esters,[15] and vinyl ketones[16] to give ortho-substituted arylalkenes. Further, a method for the regiospecific attachment of carbon nucleophiles to the β carbon of allylic sulfides and amines using palladium complexes recently has been developed.[17]

In this paper we describe reactions of cyclometalation products (**1**) of azobenzene,[6] tertiary benzylic amines,[18,19] and



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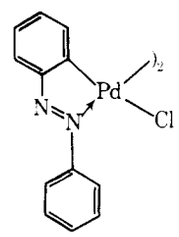
Schiff bases[20,21] with either organolithium compounds or Grignard reagents, which provide a convenient method for synthesis of ortho-substituted aromatic compounds and give important mechanistic insight into the carbon–carbon bond formation via palladium complexes.[22]

Results and Discussion

The Reaction of the Complex 1 with Alkyllithium Compounds or Grignard Reagents. The reactions of cyclometallation products **1**, such as di-μ-chloro-bis[2-(phenylazo)phenyl]dipalladium (**2**), di-μ-chloro-bis[2-(*N*,*N*-dimethylaminomethyl)phenyl]dipalladium (**3**), and di-μ-chloro-bis[2-(*N*-phenylformimidolyl)phenyl]dipalladium (**4**), with alkyllithium compounds were carried out in ether at 0–5 °C under heterogeneous conditions. Treatment of **2** with methyllithium produced 2-methylazobenzene (**5b**) and azobenzene (**5a**) in 55 and 45% yields, respectively. The similar reaction of **2** with phenyllithium gave **5c** (42%) and **5a** (58%).



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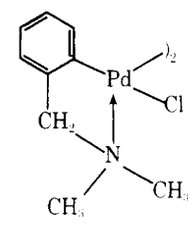

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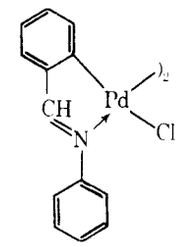

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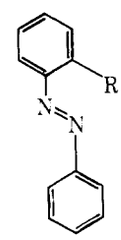
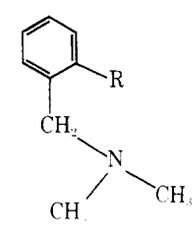
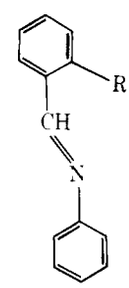


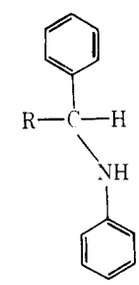
5a, R = H
b, R = CH_3
c, R = C_6H_5
d, R = C_4H_9



6a, R = H
b, R = CH_3
c, R = $CH{=}CH_2$
d, R = C_2H_5
e, R = C_4H_9



7a, R = H
b, R = CH_3
c, R = t-C_4H_9
d, R = C_6H_5
e, R = C_4H_9



8a, R = t-C_4H_9
b, R = C_6H_5
c, R = C_4H_9

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Table I. Reaction of the Complexes 2–4 with Alkyllithium Compounds and Grignard Reagents[a]

complexes	RLi or RMgBr	product yield,[b] % ortho-substituted products	reductive products	addition products
2	CH_3Li	**5b** (55)	**5a** (44)	
2	C_6H_5Li	**5c** (42)	**5a** (58)	
2	n-C_4H_9Li	**5d** (5)	**5a** (89)	
3	CH_3Li	**6b** (49)	**6a** (47)	
3	CH_2=$CHMgBr$	**6c** (44)	**6a** (31)[c]	
3	C_2H_5MgBr	**6d** (2)	**6a** (80)	
3	n-C_4H_9Li	**6e** (5)	**6a** (80)	
4	CH_3Li	**7b** (76)	**7a** (21)	
4	t-C_4H_9Li	**7c** (28)	**7a** (34)	**8a** (14)
4	C_6H_5Li	**7d** (22)		**8b** (48)
4	C_6H_5MgBr	**7d** (28)		**8b** (28)
4	n-C_4H_9Li	**7e** (1)		**8c** (64)

[a] Palladium complex (5.5 mmol) was reacted with organolithium compounds (13 mmol) in ether at room temperature for 3–4 h. [b] VPC yield using internal standard. [c] Additional product was 6d (13%).

Table III. Effect of Ligands for the Reaction of 2 with Methyllithium[a]

ligand (L)	product yield, % compd **5b**	compd **5a**
none	55	45
PPh_3	91	0
$P(OPh)_3$	2	0
$P(n$-$Bu)_3$	56	11
$(Ph_2PCH_2)_2$	18	0

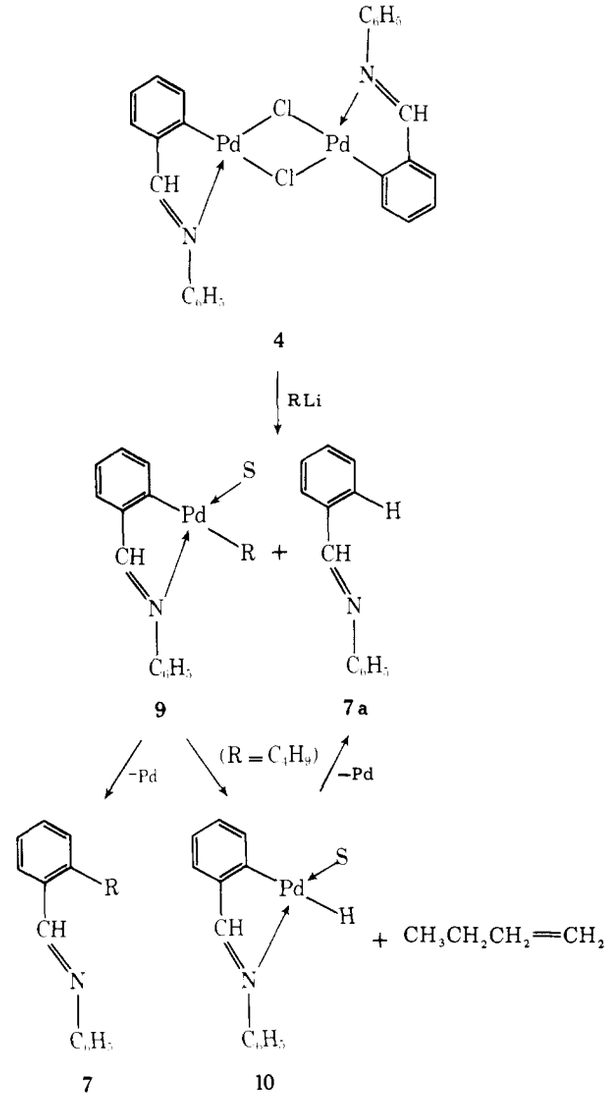
[a] To the suspension of **2** (0.5 mmol) and PPh_3 (2.0 mmol) in benzene was added an ethereal solution of methyllithium (1.0 mmol).

The structures of the products were established either by comparison of spectral data with those of authentic samples or by elemental analyses and spectral data as summarized in Table II (see supplementary material). The ortho-substituted products **5b** or **5c** and reductive product **5a** were each obtained in approximately 50% yield. On the contrary, **5a** was obtained almost exclusively (89%) along with a small amount of **5d** (5%) upon treatment with n-butyllithium.

Similar reactions of complexes **3** and **4** with alkyllithium compounds also gave the corresponding 1-alkyl-substituted benzylamines (**6**) and Schiff bases (**7**), respectively, as shown in Table I. o-(*tert*-Butyl)benzaldehyde was prepared upon treatment of **4** with *tert*-butyllithium followed by acid hydrolysis in 25% yield. The previous method for synthesis of this aldehyde required six steps, and the yield was poor.[23] The ortho alkylation products of **4** are sometimes contaminated with N-(α-substituted)benzylaniline (**8**), derived from the addition of alkyllithium compounds into the carbon–nitrogen double bond of the Schiff bases. Grignard reagents also react with these complexes. Thus, treatment of **3** with vinylmagnesium bromide gave **6a** (31%), **6c** (31%), and **6d** (13%).

The reaction of complex **4** with alkyllithiums can be envisioned to occur by Scheme I. The first step would be nucleophilic substitution of the chloride group by the alkyllithium, giving intermediate **9** accompanied by splitting of the bridge structure to liberate **7a**.[24] Subsequent reductive coupling of **9** would produce **7**. The predominant formation of **7a** upon treatment with n-butyllithium is consistent with this scheme. Butylpalladium complex **9** (R = C_4H_9) undergoes facile β elimination of a palladium hydride species[26] to give the hydride complex **10**, which is the precursor of **7a**.

Scheme I



The Reaction of Complex 1 with Organolithium Compounds or Grignard Reagents in the Presence of Triphenylphosphine. In view of selective syntheses of ortho-substituted **5** from **2**, the loss of the one part of azobenzene upon treatment with alkyllithium must be avoided. Should the reaction proceed as depicted in Scheme I, the preliminary splitting of **2** into two phosphine-coordinated monomer complexes[21,27] is necessary.

For this reason, chloro[2-(phenylazo)phenyl]bis(triphenylphosphine)palladium (**23**) was prepared by treatment of **2** with excess triphenylphosphine in methanol (86% yield). The methylation reaction of **23** with methyllithium in benzene/ether gave **5b** in 98% yield. Moreover, the reaction of **2** with methyllithium in the presence of 4 molar equiv of triphenylphosphine gave **5b** in 91% yield, indicating that the isolation of **23** is unnecessary. A similar reaction of **3** with methyllithium in the presence of 4 equiv of triphenylphosphine afforded 2-methyl-*N*,*N*-dimethylbenzylamine in 99% yield. Further, the reaction of **4** with methyllithium followed by acid hydrolysis gave o-methylbenzaldehyde (**14**) in 95% yield. A study of the ligand effect on the reaction of **2** with methyllithium showed that triphenylphosphine gave the best result among the ligands examined, as shown in Table III.

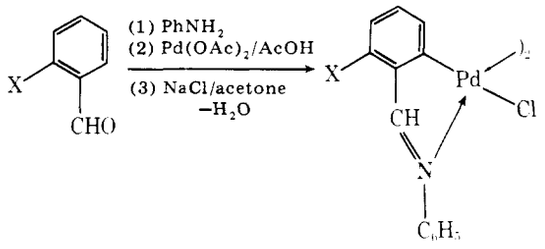
If the reaction is performed twice on the cyclometallation products, 2,6-dialkyl-substituted aromatic compounds, which are difficultly accessible, can be prepared readily. In anticipation of this double treatment, Schiff base–palladium complexes of ortho-substituted benzaldehydes, **11–13**, were

Table IV. Reaction of Palladium Complexes of Schiff Bases with Organolithium Compounds or Grignard Reagents in the Presence of Triphenylphosphine[a]

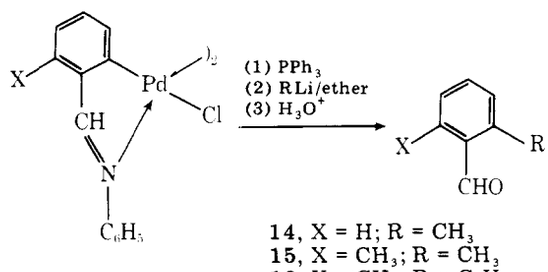
complexes[b]	RLi (RMgX)	ratio of PPh_3/Pd	products[c]	yield,[d] %
2	CH_3Li	4	**5b**	91
3	CH_3Li	4	**6b**	99
4	CH_3Li	2	**14**	90
4	CH_3Li	4	**14**	95
11	CH_3Li	4	**15**	86
11	CH_3MgX[e]	4	**15**	70
11	C_3H_7Li	4	**19**	90
11	C_4H_9Li	4	**16**	75
11	C_6H_5Li	4	**17**	60
12	CH_3Li	4	**21**	85
13	CH_3Li	4	**22**	60

[a] A mixture of palladium complex (0.5 mmol) and PPh_3 (2.0 mmol) was used with organolithium compounds (1.0 mmol) in ether at room temperature. [b] Complexes can be prepared in over 95% yield. [c] Obtained by acid hydrolysis. [d] Based upon the palladium complexes of Schiff bases. [e] A 4 molar equiv amount of CH_3MgX was reacted.

synthesized since the expected products, 2,6-disubstituted benzaldehydes, are difficultly accessible, useful compounds. The reaction of Schiff bases, derived from the corresponding aldehydes and aniline quantitatively, with equimolar quantities of palladium acetate in acetic acid at reflux followed by treatment with sodium chloride gave the expected palladium complexes in 95–96% yields. The methylation of di-μ-chloro-bis[*o*-(*N*-phenylformimidoyl)-2-methylphenyl]dipalladium (**11**) with methyllithium in the presence of 4 molar equiv of triphenylphosphine followed by hydrolysis gave 2,6-dimethylbenzaldehyde (**15**)[28] in 86% yield. The yield of **15** is dependent upon the added ligand in the order of $P(n\text{-}C_4H_9)_3$ (3%) < none (12%) < $P(OC_6H_5)_3$ (26%) < $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (75%) < $P(C_6H_5)_3$ (86%), indicating that triphenylphosphine is best. Other examples of the synthesis of 2,6-disubstituted benzaldehydes are summarized in Table IV. The structural assignment of these products was established by mass, IR, and NMR spectral data as shown in Table II. Unexpectedly, 2,6-disubstituted benzaldehydes **16–22** are unknown compounds, indicating the difficulty of their synthesis.[29] Grignard reagents are also applicable to this reaction; however, in this case the presence of 4 molar equiv of triphenylphosphine and the Grignard reagents is required because of the lower nucleophilicity of Grignard reagents in comparison with alkyllithiums. Actually, the yield of **15** from **11** decreased to 70% when methylmagnesium bromide was used instead of methyllithium. Acetate ligands can be replaced as well as chloride ligand. Thus, the reaction of di-μ-acetato-bis[2-(*N*-phenylimidoyl)-6-methylphenyl]dipalladium with methyllithium in the presence of PPh_3 followed by hydrolysis afforded **15** in 90% yield.



4, X = H (yellow)
11, X = CH_3 (yellow)
12, X = OCH_3 (yellow)
13, X = Cl (green)



14, X = H; R = CH_3
15, X = CH_3; R = CH_3
16, X = CH_3; R = C_4H_9
17, X = CH_3; R = C_6H_5
18, X = CH_3; R = $CH(CH_3)_2$
19, X = CH_3; R = C_3H_7
20, X = CH_3; R = $CH(CH_3)CH_2CH_3$
21, X = OCH_3; R = CH_3
22, X = Cl; R = CH_3

Table V. Ligand Effect of Triphenylphosphine in the Reaction of Palladium Complex 11 with *n*-Propyllithium or *n*-Butyllithium

alkyllithium	relative ratio of PPh_3/Pd	products,[a] (yield, %)
$n\text{-}C_3H_7Li$	0	**19** (10), **14** (73)
	2	**19** (37), **14** (45)
	4	**19** (90), **14** (9)
	8	**19** (68), **14** (1)
$n\text{-}C_4H_9Li$	0	**16** (5), **14** (91)
	4	**16** (75), **14** (4)

[a] Products were analyzed after acid hydrolysis.

Selective ortho alkylation of **11** can be depicted as shown in Scheme II. Dimeric palladium complex **11** can be converted into 2 mol of the phosphine-coordinated palladium complex **24** upon treatment with 4 equiv of PPh_3. The reaction with alkyllithium would lead to the σ-alkylarylpalladium complex **26** by nucleophilic substitution with the carbon nucleophile at the palladium of **24**. Actually, Parshall has isolated $FC_6H_4PdR(PEt_3)_2$, in which there are two C-bonded ligands, by the reaction of phenyl or methyl Grignard reagents with $FC_6H_5PdBr(PEt_3)_2$.[30] An alternative process leading to complex **26** may be substitution via palladium ate complex **25**.[31,32] Facile reductive coupling[30,33,34] of **26** would lead to **28**, which is the precursor of **14**.

In the case of the reaction of alkyllithiums bearing β hydrogens, the β elimination of **26** accompanied by loss of an alkene would lead to palladium hydrido complex **27**, which would readily undergo reductive coupling to give **29**. Indeed, when butyllithium was reacted with complex **11** in the presence of 4 equiv of triphenylphosphine, the desired 2-methyl-6-butylbenzaldehyde (**16**) was obtained in 75% yield along with the reductive coupling product, 2-methylbenzaldehyde (**14**; 9%). In the absence of PPh_3, however, **16** and **14** were obtained in 10 and 90% yields, respectively. The addition of PPh_3 retards the β elimination of the palladium hydride species in **26** drastically. The best yield of **19**, for example, was obtained when the relative ratio of triphenylphosphine to palladium was 4, as indicated in Table V. This is presumably due to an increase of stability of the σ-alkylpalladium intermediate **26** by coordination with PPh_3.[35] It is well known that phosphine ligand facilitates the π–σ conversion of π-allylpalladium chloride complexes.[36]

Secondary alkyllithium compounds also undergo the cross-coupling reaction, accompanied by alkyl group isomerization from secondary to primary.[37] The reaction of **11** with isopropyllithium in the presence of 2 molar triphenylphosphine followed by hydrolysis gave 2-methyl-6-isopropylbenzaldehyde (**18**; 6%), 2-methyl-6-propylbenzaldehyde (**19**; 5%), and 2-methylbenzaldehyde (**14**; 85%). Likewise, the reaction

of 11 with 1-methylpropyllithium afforded 2-methyl-6-(1-methylpropyl)benzaldehyde (**20**; 10%), 2-methyl-6-butylbenzaldehyde (**16**; 6%), and **14** (70%). The yields of alkylation products **16** and **18–20** depend upon the amount of phosphine ligand present. Reactions of primary alkyllithium compounds (Table V) are more strongly influenced than those of secondary alkyllithiums (Table VI). It is noteworthy that bidentated 1,2-bis(diphenylphosphino)ethane gave a relatively good result.

The initially formed complex **32**, bearing the Pd–$CH(CH_3)R$ bond, undergoes reductive coupling to give **30** (Scheme III). The rapid isomerization from secondary to primary alkylpalladium (**34**) proceeds via a hydride–olefin intermediate (**33**), a precursor of **14** as shown in Scheme IV. For the formation of **14** from **11**, an alternative process involving protonolysis[30] or homolytic cleavage of the Pd–C bond,[38] leading to a phenyl radical which abstracts hydrogen, was excluded by the following results. Although protonolysis of **11** with DCl[39] in benzene/D_2O gave 2-deuterio-6-methylbenzaldehyde, an NMR study showed that the H^2 proton of **14**, obtained from the reaction of **11** with isopropyllithium in the presence of PPh_3 followed by quenching with DCl, contained 0.10 *d*, indicating that only 10% of **14** was formed by protonolysis. The pyrolysis of **11** in benzene-d_6 gave **14**, whose H^2 proton contained only 0.04 *d*.

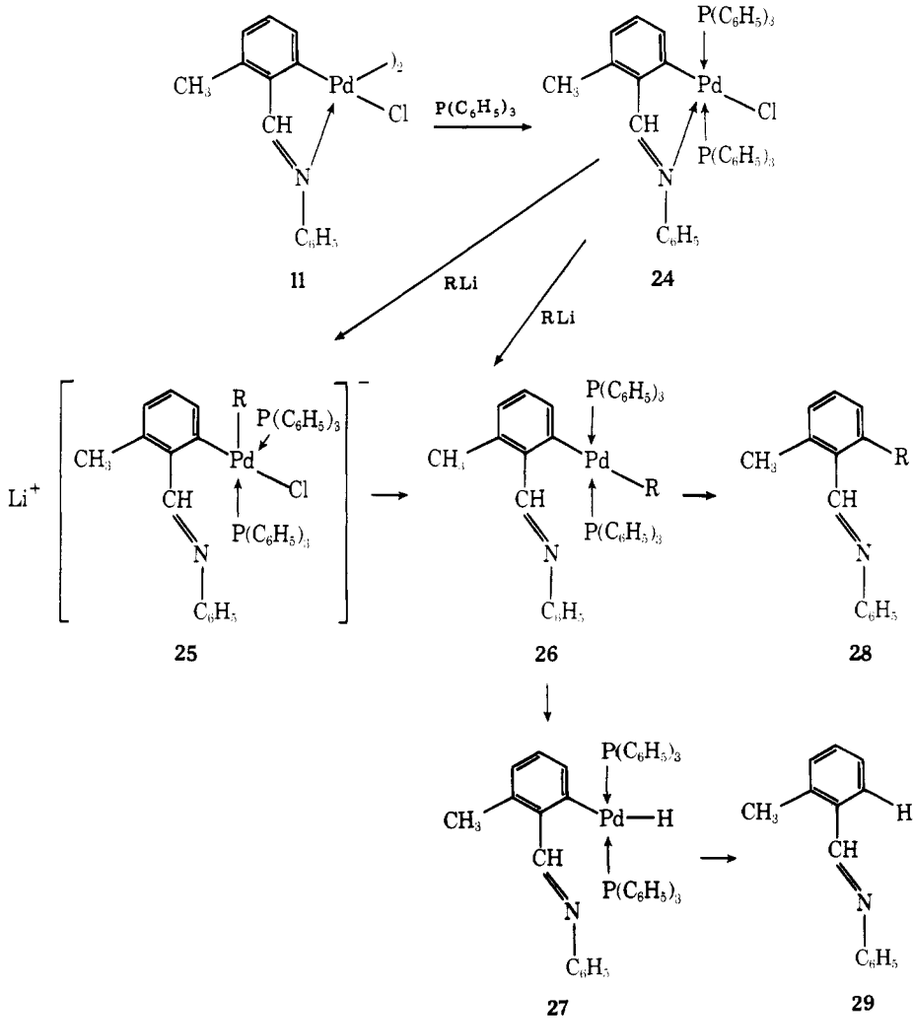
The reaction of **11** with propyllithium in the presence of PPh_3 gave **19** and **14** in 37 and 45% yields, respectively; however, none of the isomerized product **18** could be detected among the products. This may be due to the release of steric strain between the branched alkyl chain and the phenyl rings of the triphenylphosphine ligands rather than an electronic effect. An increase in the electron density on palladium owing to the electron-donating ligand seems not to facilitate the σ–π conversion.[35,36] The extent of the isomerization in the reaction of **11** with isopropyllithium was independent of the ligands used as seen from the results shown in Table VI. The present

Table VI. Reaction of Palladium Complex 11 with *sec*-Alkyllithiums[a]

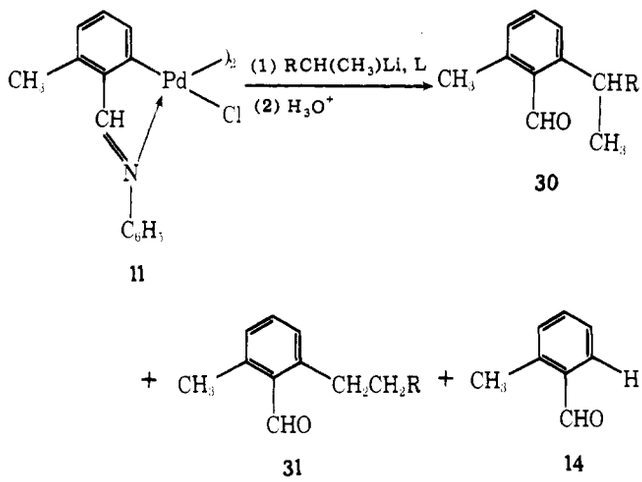
$R(CH_3)CHLi$, R	ligand (L)	relative ratio L/Pd	product,[b] (yield, %)[c]
CH_3	none		**18** (0), **19** (0), **14** (96)
CH_3	PPh_3	1	**18** (5), **19** (6), **14** (68)
CH_3	PPh_3	2	**18** (6), **19** (5), **14** (85)
CH_3	PPh_3	4	**18** (15), **19** (8), **14** (14)
CH_3	PPh_3	8	**18** (24), **19** (7), **14** (20)
CH_3	PPh_3	16	**18** (30), **19** (8), **14** (5)
CH_3	PBu_3	1	**18** (4), **19** (2), **14** (90)
CH_3	PBu_3	2	**18** (7), **19** (4), **14** (59)
CH_3	PBu_3	4	**18** (11), **19** (4), **14** (22)
CH_3	$Ph_2CH_2CH_2PPh_2$	2	**18** (18), **19** (8), **14** (15)
CH_3	$P(OPh)_3$	2	**18** (9), **19** (8), **14** (80)
CH_2CH_3	none		**20** (1), **16** (0), **14** (65)
CH_2CH_3	PPh_3	2	**20** (10), **16** (6), **14** (70)

[a] *sec*-Alkyllithiums were added to an equimolar amount of complex **11** in the presence of a ligand in benzene/hexane at room temperature. [b] Obtained by acid hydrolysis. [c] VPC yield.

Scheme II

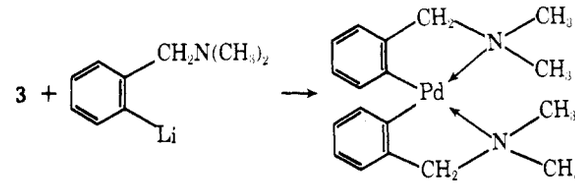


Scheme III



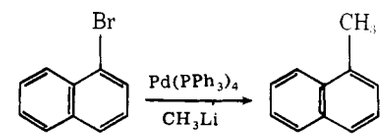
work is the first example of isomerism in palladium alkyls which are in thermal equilibrium. Generally, β elimination of palladium hydride species from alkylpalladium compounds proceeds readily to give alkenes.[26] Similar alkyl group isomerizations have been reported in alkyliridium,[40] -nickel,[41,42] -gold,[43] and -titanium[44] complexes. It is noteworthy that the isomerization of secondary alkylnickel complexes to primary alkyls is strongly dependent upon the electronic nature of the phosphine ligand.[41]

To determine the effect of a carbon ligand toward the cross-coupling reaction, *cis*-bis[2-(*N*,*N*-dimethylaminomethyl)phenyl]palladium (**35**) was prepared by the reaction of **3** with *o*-lithio-*N*,*N*-dimethylbenzylamine in 33% yield. This complex is identical with the cis complex previously formed from bis(dimethyl sulfide)palladium dichloride and 2 mol of *o*-lithio-*N*,*N*-dimethylamine.[45] The methylation of **35** with methyllithium gave **6b** in only 8% yield along with **6a** (90%). The addition of PPh_3 increases the yield of **6b** by the coordination of phosphine to palladium rather than the chelating of nitrogen of **35**, which stabilizes the $ArPdCH_3L_n$ intermediate. Thus, in the presence of 2 mol of PPh_3, the same reaction gave **6b** in 35% yield in addition to **6a** (60%). In

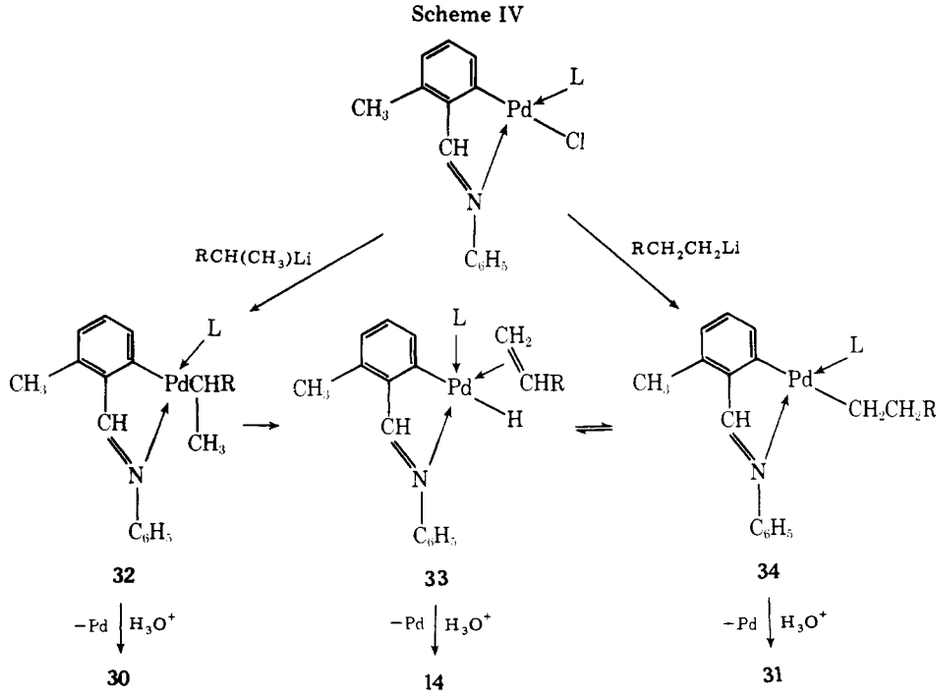


comparison with the methylation of **3**, where **6b** was obtained in 49 or 99% yield, in the absence or presence of PPh_3, respectively, the yield of the methylation products of **35** is rather low. This may be attributed to the replacement of the methyl moiety of methyllithium with one of the aryl groups of **35** via an unstable palladium ate complex, yielding *o*-lithio-*N*,*N*-dimethylbenzylamine[32] or 2-(*N*,*N*-dimethylmethyl)phenyl radical,[46] both of which are precursors of **6a** if the reaction proceeds by Scheme II. Arylpalladium complexes generally have about the same stability as the methyl analogues.[35,38]

The reaction involves intermediacy of arylalkylpalladium species formed by nucleophilic attack of a carbon nucleophile on palladium in the arylpalladium complex. In support of this mechanism, alkyl isomerization from secondary to primary occurs under the reaction conditions. Furthermore, this alkylation proceeds only in the case of the harder carbon nucleophiles, such as alkyllithium or Grignard reagents, but not in the case of softer carbanions, which have been shown to attack carbon directly on the face of the olefin[47] and π-allyl units[48] opposite to that of palladium. Actually, arylpalladium species derived from oxidative addition[30,49] of aryl halides to zerovalent palladium complexes react with alkyllithium compounds, producing the corresponding coupling products, although for simple alkylations the nickel-catalyzed cross coupling with Grignard reagents[50,51] seems more practical. Treatment of α-bromonaphthalene with 1 equiv of tetrakis(triphenylphosphine)palladium in benzene at reflux followed

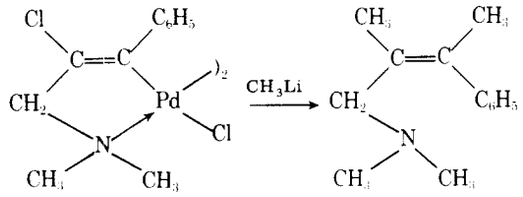


Scheme IV



by addition of methyllithium gave α-methylnaphthalene in 90% yield. Similarly, β-bromonaphthalene was converted into β-methylnaphthalene in 88% yield.

Finally, for comparison with the σ-aryl metalocyclic palladium complexes, σ-vinyl metalocyclic palladium complexes were subjected to the alkylation reaction, aiming at the stereoselective synthesis of allylamines. However, preliminary results with the methylation of di-μ-chloro-bis(2-chloro-3-*N*,*N*-dimethylamino-1-phenylpropenyl)dipalladium (**36**)[52] showed that it proceeded nonstereoselectively. Thus, treatment of **36** with 4 equiv of methyllithium gave *N*,*N*-dimethyl-*cis*-α,β-cinnamylamine (*cis*-**37**), the trans isomer (*trans*-**37**), and 3-(*N*,*N*-dimethylamino)-3-methylbut-1-yne in a relative ratio of 81:11:8, indicating that complicated processes are involved.



36 **37**

In summary, the reaction of ortho palladation products with organolithium compounds in the presence of triphenylphosphine provides direct access to 2- and 2,6-substituted azobenzenes, *N*,*N*-(dimethylaminomethyl)benzenes, and benzaldehydes, which are difficultly accessible. In most instances, these new methods are a marked improvement over existing methods[53] and should find application in the synthesis of complex molecules.

Experimental Section

All melting points are uncorrected. IR spectra were recorded on a Hitachi 215 spectrometer. The NMR spectra were obtained on a JNM-4H spectrometer, and chemical shifts are reported in δ values downfield from the internal standard tetramethylsilane. Mass spectra were taken on a Hitachi RSM-4 mass spectrometer. Vapor-phase chromatography was carried out with a Jeol-20K by using a 1 m analytical column packed with Carbowax 20M on Chromosorb or a 1 m column packed with Apieason L.

Di-μ-chloro-bis[2-(phenylazo)phenyl]dipalladium (2). This material was prepared by the method of Cope.[5]

Di-μ-chloro-bis[2-(*N*,*N*-dimethylaminomethyl)phenyl]dipalladium (3). The preparation of this compound has also been described by Cope.[6]

Di-μ-chloro-bis[2-(*N*-phenylformimidoyl)phenyl]dipalladium (4). This complex was prepared by the procedure of Onoue and Moritani.[20]

Reactions of Complex 2 with Organolithium Compounds. The following procedures are typical of those used to obtain the data in Table I.

(a) To a suspension of **2** (3.5 g, 5.5 mmol) in ether (30 mL) was added a solution of methyllithium (16.5 mmol) in ether (100 mL) with stirring. After continuous stirring for 4 h, the precipitated palladium black was filtered and the ether solution was treated with water and dried over $MgSO_4$. Distillation [bp 110–113 °C (1.5 mmHg)] gave red crystalline material (1.95 g) which was shown to contain azobenzene (**5a**; 44%) and 2-methylazobenzene (**5b**; 55%) by VPC analysis.

(b) Complex **2** (3.5 g, 5.5 mmol) was reacted with phenyllithium (13.5 mmol) in ether (50 mL). The products were subjected to chromatography on alumina. Elution with a mixture of petroleum ether/benzene gave biphenyl (0.6 g, 42 mmol), azobenzene (1.1 g, 58%), and 2-phenylazobenzene (**5c**; 1.2 g, 42%).

(c) To a suspension of **3** (3.0 g, 5.4 mmol) in ether was added a solution of vinylmagnesium bromide (16.0 mmol) in THF (15 mL) with stirring. After additional stirring for 1 h, the reaction mixture was heated at reflux for 30 min. Palladium black was filtered and washed with ether. The filtrate was extracted with ether. The ether extract was washed with water and dried over $MgSO_4$. Removal of the solvent followed by distillation gave 1.29 g of an oil [bp 80–100 °C (67 mmHg)] which contained **6a** (43%),[25] **6b** (13%), and **6c** (31%).

(d) To a suspension of **4** (3.3 g, 5.1 mmol) in ether (50 mL) was added a solution of phenyllithium (10.8 mmol) in ether (30 mL) with stirring. After additional stirring for 5 h, the reaction mixture was treated similarly as described in c. Distillation [140–165 °C (2 mmHg)] gave the products (2.28 g). Preparative VPC gave **7d** (22%) and *N*-phenyl-α-phenylbenzylamine (**8d**; 48%): mass spectrum, *m/e* 250 (M^+); IR ν (N–H) 3400 cm^{-1}.

Chloro[2-(phenylazo)phenyl]bis(triphenylphosphine)palladium (23). A suspension of di-μ-chloro-bis[2-(phenylazo)phenyl]-dipalladium (**2**) (0.64 g, 1 mmol) and triphenylphosphine (1.05 g, 4 mmol) in methanol (20 mL) was stirred for 8 h. Filtration followed by washing with a small amount of methanol gave 0.64 g of **23** (86%), mp 176–178 °C dec. Anal. Calcd for $C_{48}H_{39}N_2ClP_2Pd$: C, 68.02; H, 4.61; N, 3.39; Cl, 4.19. Found: C, 68.67; H, 4.46; N, 3.33; Cl, 4.43.

Reaction of Complex 23 with Methyllithium. To a suspension of **23** (0.74 g, 1.0 mmol) in dry benzene (14 mL) was added methyllithium (0.8 mL, 1.0 mmol) in ether under nitrogen. After additional stirring for 1 h, water was added. The ethereal extract was dried over $MgSO_4$ and subjected to VPC analysis (Carbowax 20M) using naphthalene as an internal standard, which showed that 2-methylazobenzene[54] was obtained in 98% yield.

Reaction of Di-μ-chloro-bis[2-(phenylazo)phenyl]dipalladium (2) with Methyllithium in the Presence of a Phosphine Ligand. A mixture of **2** (0.32 g, 0.5 mmol) and PPh_3 (0.52 g, 2.0 mmol) in benzene (15 mL) was stirred under nitrogen for 30 min at room temperature. To the resulting suspension was added an ethereal solution of methyllithium (0.8 mL, 1.0 mmol) with stirring, and the mixture was stirred for 1 h. The reaction mixture was poured into water and filtered off. The ethereal extract of the filtrate was washed with water and dried over $MgSO_4$. Filtration followed by evaporation gave 2-methylazobenzene (**5b**). The yield was determined to be 91% by VPC analysis (Carbowax 20M) using naphthalene as an internal standard. A similar reaction in the presence of other ligands was carried out, and the results are summarized in Table III.

Reaction of Di-μ-chloro-bis[2-(*N*,*N*-dimethylaminomethyl)phenyl]dipalladium (3) with Methyllithium in the Presence of Triphenylphosphine. A mixture of **3** (0.28 g, 0.5 mmol) and PPh_3 (0.52 g, 2.0 mmol) in benzene (15 mL) was stirred under nitrogen at room temperature for 30 min. A solution of methyllithium in ether (1.0 mmol, 0.8 mL) was added, and the mixture was stirred for 1 h at room temperature. The reaction mixture was poured into water and filtered. The ethereal extract was washed with water and dried over $MgSO_4$. Evaporation of the solvent gave 2-methyl-*N*,*N*-dimethylbenzylamine. The yield was determined to be 99% by VPC analysis: mass spectrum, *m/e* 149; NMR (CCl_4) δ 2.20 (s, 6 H), 2.33 (s, 3 H), 3.33 (s, 2 H), 7.04 (m, 4 H).

Reaction of Di-μ-chloro-bis[2-(*N*-phenylformimidoyl)phenyl]dipalladium (4) with Methyllithium in the Presence of Triphenylphosphine. A mixture of **4** (0.33 g, 0.50 mmol) and PPh_3 (0.52 g, 20 mmol) in benzene was stirred under nitrogen at room temperature for 30 min. To the resulting suspension was added ethereal methyllithium (1.0 mmol, 1 mL). After additional stirring for 1 h, water (20 mL) was added with stirring. The mixture was filtered off. The ethereal extract was washed with water, dried over $MgSO_4$, and distilled. VPC analysis showed that the yield of *N*-(2-methylbenzylidene)aniline was 95%: mass spectrum, *m/e* 195; NMR ($CDCl_3$) δ 2.52 (s, 3 H), 6.92–7.50 (m, 9 H), 8.65 (s, 1 H).

Di-μ-chloro-bis[2-(*N*-phenylimidoyl)-3-methylphenyl]dipalladium (11). A mixture of *N*-(2-methylbenzylidene)aniline (1.95 g, 10 mmol) and palladium acetate (2.24 g, 10 mmol) in acetic acid (50 mL) was heated at reflux for 1 h with stirring. The color of the reaction mixture changed from brown to green-yellow. After cooling to room temperature, addition of water followed by filtration gave di-μ-acetato-bis[2-(*N*-phenylimidoyl)-6-methylphenyl]dipalladium quantitatively: mp 220–224 °C dec; IR (Nujol mull) 1600, 1582 (C=N), 1568, 1418, 790, 766, 759, 720 cm^{-1}; NMR ($CDCl_3$) δ 1.73 (s, 3 H), 2.37 (s, 3 H), 6.53–7.43 (m, 4 H), 7.88 (s, 1 H). Anal. Calcd for $C_{32}H_{30}N_2O_4Pd_2$: C, 53.43; H, 4.20; N, 3.89. Found: C, 53.25; H, 4.21; N, 3.75.

The complex was dissolved in methylene chloride (20 mL), and the solution was vigorously shaked with a saturated sodium chloride solution in a mixture of water (30 mL) and acetone (20 mL). Filtration of the precipitated green-yellow crystalline compound and washing with ethanol, benzene, and methylene chloride gave **11** (3.41 g) in 95% yield: mp 260–270 °C dec; IR (Nujol mull) 1570 cm^{-1} (C=N). Anal. Calcd for $C_{28}H_{24}Cl_2N_2Pd_2$: C, 50.00; H, 3.57; N, 4.17. Found: C, 50.36; H, 3.34; N, 4.11.

Di-μ-chloro-bis[2-(*N*-phenylimidoyl)-3-methoxyphenyl]dipalladium (12). This complex (yellow) was prepared from *N*-(2-methoxybenzylidene)aniline in 94% yield as described in the synthesis of **11**: mp 230–235 °C dec; IR (Nujol mull) 1580 cm^{-1} (C=N). Anal. Calcd for $C_{28}H_{24}Cl_2N_2O_2Pd_2$: C, 47.70; H, 3.44; N, 3.98. Found: C, 47.94; H, 3.48; N, 3.79.

Di-μ-chloro-bis[2-(*N*-phenylimidoyl)-3-chlorophenyl]dipalladium (13). This green complex was prepared from *N*-(2-chlorobenzylidene)aniline in 96% yield as described in the synthesis of **11**: mp 278–280 °C dec; IR (Nujol mull) 1580 cm^{-1} (C=N). Anal. Calcd for: $C_{26}H_{18}Cl_4N_2Pd_2$: C, 43.80; H, 2.54; N, 3.93. Found: C, 43.68; H, 2.44; N, 3.87.

Reaction of Organolithium Compounds with Complex 11 in the Presence of a Ligand. In a typical case, a mixture of **11** (0.335 g, 0.5 mmol) and triphenylphosphine (0.520 g, 2.0 mmol) in benzene (15 mL) was stirred for 30 min at room temperature. To the resulting suspension was added an ethereal solution of methyllithium (0.8 mL, 1.0 mmol) with stirring for 1 h, during which time the color of the reaction mixture changed from yellow to green-yellow. After addition of hydrochloric acid (1 N, 15 mL) with stirring for 1 h, the mixture was filtered off. The ethereal extract was dried over $MgSO_4$ and distilled. VPC analysis (SE 20) of the distillate using an internal standard of dibenzyl showed that the product consisted of 2,6-dimethylbenzaldehyde (**15**; 86%) and 2-methylbenzaldehyde (**14**; 10%). The ligand effect concerning in this methylation was also investigated under the same reaction conditions. The results are summarized in Table V. The structural assignment of the products was made by the spectral data shown in Table II and by elemental analyses.

The reactions of **11** with *sec*-alkyllithiums were carried out similarly. The results are summarized in Table VI. The ligand effect toward the reaction of **11** with isopropyllithium is also shown in Table VI.

2-Deuterio-6-methylbenzaldehyde. A mixture of complex **11** (0.180 g, 0.25 mmol) and PPh_3 (0.260 g, 1.0 mmol) in benzene (8 mL) was stirred for 30 min. To the resulting suspension, DCl/D_2O, prepared by the treatment of acetyl chloride (2 mL) with D_2O (10 mL), was added with stirring at room temperature for 1 h. Filtration, ether extraction, and distillation gave 2-deuterio-6-methylbenzaldehyde. A pure sample was collected by preparative VPC (SE 30, 120 °C): NMR (CCl_4) δ 2.63 (s, 3 H), 7.03–7.43 (m, 3 H), 10.12 (s, 1 H). The absorption corresponding to the ortho H (δ 7.60–7.87) disappeared.

Quenching the Product from 11 and Isopropyllithium with DCl/D_2O. The complex **11** was reacted with isopropyllithium under the reaction conditions described above. The reaction mixture was quenched with DCl/D_2O, and 2-methylbenzaldehyde (**14**) was collected by VPC (SE 30, 120 °C). The NMR spectrum of **14** indicated that the content of 2-deuterio-6-methylbenzaldehyde was 10%.

The Reaction of 11 with Isopropyllithium in Benzene-d_6. The complex **11** (0.18 g, 0.025 mmol) was allowed to react with isopropyllithium (0.025 mmol) in benzene-d_6 (7 mL) in the presence of PPh_3 (0.26 g, 1.0 mmol). The NMR analysis of 2-methylbenzaldehyde, collected by VPC as described above, showed that the number of protons of the ortho position was 0.96, indicating that the deuterium abstraction from benzene-d_6 under the reaction conditions is negligible.

Bis[2-(*N*,*N*-dimethylaminomethyl)phenyl]palladium (35). A solution of *o*-lithio-*N*,*N*-dimethylbenzylamine, prepared by treatment of *N*,*N*-dimethylbenzylamine (0.135 g, 1 mmol) with *n*-butyllithium (1 mmol) in ether under nitrogen, was added to a suspension of di-μ-chloro-bis[2-(*N*,*N*-dimethylaminomethyl)phenyl]dipalladium (**3**; 0.275 g, 0.5 mmol) in ether with stirring at room temperature. After additional stirring for 1 h, addition of water (2 mL), filtration, and washing with water gave the complex **35**. Recrystallization from THF gave analytically pure white needles of **35** (0.124 g, 33%): mp 221 °C dec (lit.[45] mp 180–210 °C); IR (Nujol mull) 1589, 738 cm^{-1}; NMR ($CDCl_3$) δ 2.63 (s, 6 H), 3.88 (s, 2 H), 6.93–7.77 (m, 4 H). Anal. Calcd for $C_{18}H_{24}N_2Pd$: C, 57.68; H, 6.43; N, 7.47. Found: C, 57.53; H, 6.47; N, 7.46.

Reaction of Complex 35 with Methyllithium. To a mixture of complex **35** (0.0187 g, 0.05 mmol) and PPh_3 (0.0524 g, 0.2 mmol) in ether was added an ethereal solution of methyllithium (0.08 mL, 0.10 mmol). After the standard treatment as mentioned above, the products were subjected to VPC analysis, indicating that **6b** (0.035 mmol, 35%) and **6a** (0.060 mmol, 60%) were obtained. When the same reaction was carried out in the absence of PPh_3, **6b** and **6a** were obtained in 8 and 90% yields, respectively.

Reaction of Bromonaphthalene with Methyllithium in the Presence of Tetrakis(triphenylphosphine)palladium. A mixture of α-bromonaphthalene (0.208 g, 1.0 mmol) and tetrakis(triphenylphosphine)palladium[55] (1.155 g, 1.0 mmol) in benzene (10 mL) was heated at reflux under an argon atmosphere for 5 h. After cooling to room temperature, an ethereal solution of methyllithium (0.8 mL, 1.0 mmol) was added to the resulting yellow solution, and the mixture was stirred for 1 h. The reaction mixture was poured into water and filtered off. The filtrate was extracted with ether. The ether extract was washed with water, dried over $MgSO_4$, and concentrated. VPC analysis using an internal standard (biphenyl) showed that α-methylnaphthalene was obtained in 90% yield. A similar reaction with β-bromonaphthalene gave β-methylnaphthalene in 88% yield.

Reaction of Di-μ-chloro-bis(2-chloro-3-*N*,*N*-dimethylamino-1-phenylpropenyl)dipalladium (36) with Methyllithium. The complex **36** was prepared from 3-(*N*,*N*-dimethylamino)-3-methylbut-1-yne with lithium chloride and palladium chloride by the method of Yukawa and Tsutsumi.[52] To a suspension of **36** (3.4 g, 5 mmol) in ether (25 mL) was added methyllithium (20 mmol) in ether (23 mL) with stirring at ambient temperature for 3 h. After heating at reflux for 1 h, the reaction mixture was poured into water and filtered off. The ethereal extract was washed with water and dried over $MgSO_4$. After removal of the solvent, distillation of the residual material gave 1.6 g of the products [bp 55–60 °C (12 mmHg)]. VPC analysis showed that three compounds were obtained. The first product was *N*,*N*-dimethyl-*cis*-α,β-dimethylcinnamylamine (**37**; 81%): mass spectrum, *m/e* 189 (M^+); NMR ($CDCl_3$) δ 1.88 (s, 3 H), 1.98 (s, 3 H), 2.04 (s, 6 H), 2.73 (s, 2 H), 7.00–7.40 (m, 5 H). Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.26; H, 10.09; N, 7.35. The assignment of the stereochemistry of **37** was made by comparison with an authentic sample. The second compound was the trans isomer of **37** (11%): mass spectrum, *m/e* 189 (M^+); NMR ($CDCl_3$) δ 1.63 (s, 3 H), 2.01 (s, 3 H), 2.28 (s, 6 H), 3.03 (s, 2 H), 7.10–7.50 (m, 5 H). Anal. Found: C, 82.27; H, 10.15; N, 7.27. The last compound was 3-(*N*,*N*-dimethylamino)-3-methylbut-1-yne[56] (8%).

***N*,*N*-Dimethyl-*cis*-α,β-dimethylcinnamylamine (37).** The usual reduction of *cis*-α,β-dimethylcinnamic acid[57] (3.0 g, 17 mmol) with $LiAlH_4$ (0.60 g, 12 mmol) gave *cis*-α,β-dimethylcinnamic alcohol (2.50 g, 88%): NMR ($CDCl_3$) δ 1.83 (s, 3 H), 1.93 (s, 3 H), 2.50 (s, 1 H), 3.85 (s, 2 H), 7.2 (m, 5 H). To a mixture of the alcohol (0.80 g, 4.8 mmol), pyridine (10 mL), and ether (30 mL) was added tribromophosphine (0.45 g, 1.6 mmol) with stirring for 2 h at 0–5 °C. After additional stirring for 2 h at room temperature, ice water (20 mL) and ether (20 mL) were added. The ethereal extract was washed with water and saturated NaCl solution, dried over $MgSO_4$, and concentrated. Short-path distillation gave *cis*-α,β-dimethylcinnamyl bromide (0.88 g, 81%): NMR (CCl_4) δ 1.90 (s, 3 H), 1.95 (s, 3 H), 3.80 (s, 2 H), 7.20 (s, 5 H). The bromide (0.80 g, 3.6 mmol) was treated with dimethylamine (3.0 g, 67 mmol) in ether at 0–5 °C followed by preparative VPC (Carbowax 20 M, 150 °C) to give **37**.

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Registry No.—**2**, 14873-53-1; **3**, 18987-59-2; **4**, 20523-73-3; **5d**, 103-33-3; **5b**, 6676-90-0; **5c**, 14336-17-5; **5d**, 67292-49-3; **6a**, 103-83-3; **6b**, 4525-48-8; **6c**, 22826-55-7; **6d**, 52728-16-2; **6e**, 67292-50-6; **7a**, 538-51-2; **7b**, 10228-77-0; **7c**, 54884-52-5; **7d**, 67292-51-7; **7e**, 54884-53-6; **8a**, 67292-52-8; **8b**, 1865-12-9; **8c**, 62740-72-1; **11**, 54865-91-7; **12**, 54865-92-8; **13**, 67316-57-8; **14**, 529-20-4; **15**, 1123-56-4; **16**, 54876-93-6; **17**, 54884-54-7; 54876-90-3; **19**, 54876-91-4; **20**, 54876-92-5; **21**, 54884-55-8; **22**, 1194-64-5; **23**, 67337-39-7; **35**, 38437-97-7; **36**, 20492-75-5; *cis*-**37**, 67292-53-9; *trans*-**37**, 67292-54-0; triphenylphosphine, 603-35-0; di-μ-acetato-bis[2-(*N*-phenylimidoyl)-6-methylphenyl]dipalladium, 67316-56-7; *N*-(2-methoxybenzylidene)aniline, 3369-37-7; α-bromonaphthalene, 90-11-9; α-methylnaphthalene, 90-12-0; β-bromonaphthalene, 580-13-2; β-methylnaphthalene, 91-57-6; 3-(*N*,*N*-dimethylamino)-3-methylbut-1-yne, 19788-24-0; *cis*-α,β-dimethylcinnamic acid, 4540-79-8; *cis*-α,β-dimethylcinnamic alcohol, 21017-11-8; *cis*-α,β-dimethylcinnamyl bromide, 67292-55-1.

Supplementary Material Available: Spectral data of compounds **5b–d**, **6b–e**, **7b–e**, **10**, and **14–22** (Table II) (2 pages). Ordering information is given on any current masthead page.

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The 1-Hetera-3-cyclohexanone System. Carbon-13 Magnetic Resonance, Transannular Effects, and Conformational Analysis[1a]

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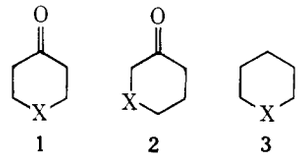
Carbon-13 (^{13}C NMR) magnetic resonance has been applied to the title compounds. Earlier suggestions[2,3] that the effects α to the heteroatom group reflect electrostatic effects and that the effects at a methylene carbon β to the heteroatom group indicate similar (chair) conformations are reinforced. The title compounds are therefore indicated to have chair conformations. Unusual heteroatom effects at the γ carbon are encountered. The groups appended to the heteroatoms are shown to have similar conformations in **1**, **2**, and **3** (under conditions of fast amide rotation). Transannular electron transfer is detected in the carbonyl chemical shifts of the thia analogue here and, to a lesser extent, in the 1-thia-4-cyclohexanone, modifying our earlier interpretation.[3] Other evidence for this transannular component is presented along with possible interpretations.

The use of carbon-13 nuclear magnetic resonance spectroscopy[2] (^{13}C NMR) as a probe[3] for conformational analysis[2-5] and transannular interactions[3] in six-membered heterocycles was evaluated in the 1-hetera-4-cyclohexanone system (**1**) in prior work. We wish herein to report an extension of this approach to the 1-hetera-3-cyclohexanone system (**2**), producing conclusions which reinforce earlier suggestions but which also require slight modification of our analysis of transannular interactions.

It has become fairly well-documented[2-6] that the effects of heteroatom groups on the α carbon reflect the heteroatom group electrostatic effects, and the 1-hetera-3-cyclohexanones (**2**) are no exception at either C-2 or C-6 (Figure 1). Plots of the chemical shifts (Table I) of the carbon resonances at C-2 and C-6 in **2** relative to the chemical shifts of the corresponding positions (α or γ to the carbonyl, respectively) in cyclohexanone ($\delta^{\alpha}_{C_5H_8XO} - \delta_{C_6H_{10}O}$) against the chemical shifts of the α carbons in the pentamethylene heterocycles[3] **3** relative



1 **2** **3**

a, X = S
b, X = N–CO–CH_3
c, X = N–CO–OR
d, X = SO_2
e, X = N–CH_2Ph
f, X = N–CH_3
g, X = O
h, X = N–CO–C_6H_5

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