diastereoisomers; mp about 200 °C; ^{31}P NMR (THF) δ 67.2 and 67.7; ^{1}H NMR (CDCl$_3$) δ 1.96 (m, $^5J_{HH}$ = 0.5, 1.35 H, C$_3$-CH$_3$ A isomer), 2.03 (m, $^5J_{HH}$ = 0.5, 1.65 H, C$_3$-CH$_3$ B isomer), 2.12 (m, $^4J_{HP}$ = 1.7) and 2.15 (m, $^4J_{HP}$ = 1.7, 3 H; C$_4$-CH$_3$ A and B), 2.27 (d, $^2J_{HP}$ = 14.6, 1.65 H, SCH$_3$ B), 2.37 (d, $^2J_{HP}$ = 14.9, 1.35 H, SCH$_3$ A), 6.02 (dm, $^2J_{HP}$ = 33.5, $^5J_{HH}$ = 0.5, 0.55, C$_5$-H B), 6.14 (dm, $^2J_{HP}$ = 33.4, 0.45 H, C$_5$-H A); ^{13}C NMR selected data (CDCl$_3$) δ 13.08 (s, CH$_3$), 15.21 (d, ^2J = 14.1) and 17.46 (d, ^2J = 18.1, SCH$_3$ A and B), 125.02 (pseudo t, ^2J = 84.4, C$_5$), 149.88 and 151.45 (m, C$_5$ A and B); mass spectrum m/z (rel intensity) 378 (M$^+$, 70), 331 (M$^+$ – SMe, 100), 299 (M$^+$ – SMe – S, 50), 220 (M$^+$ – 2SMe – 2S, 50). Anal. Calcd for $C_{14}H_{20}P_2S_4$: C, 44.43; H, 5.33; P, 16.36; S, 33.88. Found: C, 44.67; H, 5.30; P, 15.98; S, 34.03.

4,4′,5,5′-Tetramethyl-2,2′-bis(methylthio)-6,6′-bis(ethoxycarbonyl)-2,2′-diphospha-3,3′-bi[bicyclo[3.1.0]hex-3-enyl] 2,2′-Disulfide (15). To a solution of 2.0 g (5.3 × 10^{-3} mol) of diphosphole disulfide 14 in xylene (10 mL) at 150 °C was added 1.52 g (1.33 × 10^{-2} mol) of ethyl diazoacetate over 10 min. The mixture was stirred for 1 h at 150 °C and then chromatographed first with dichloromethane and then with dichloromethane/ethyl acetate (80–20): yield 1.8 g (62%); mixture of two isomers; ^{31}P NMR (xylene) δ 81.6 and 81.9. An analytical sample was recrystallized in dichloromethane, leading to one of the diastereoisomers: mp 224 °C; ^{31}P NMR (CDCl$_3$) δ 80.5; ^{1}H NMR (CDCl$_3$) δ 1.31 (t, $^3J_{HH}$ = 7.1, CH$_3$), 1.55 (s, 3 H, C$_5$-CH$_3$), 1.92 (pseudo t, 3 H, C$_4$-CH$_3$), 2.30 (d, $^3J_{HP}$ = 14.4, SCH$_3$), 2.05 and 2.46 (ABX; A part, dd, $^3J_{HH}$ = 4.7, $^3J_{HP}$ = 13.2, 1 H, C$_6$-H; B part, dd, $^3J_{HH}$ = 4.7, $^2J_{HP}$ = 12.5, 1 H, C$_1$-H), 4.20 (ABX$_3$, 2 H, OCH$_2$); ^{13}C NMR (CDCl$_3$) δ 12.28 (s, S-CH$_3$), 14.25 (s, CH$_3$), 15.86 (s, C$_5$-SCH$_3$), 16.40 (d, ^3J = 13.4, C$_4$-CH$_3$), 31.79 (d, ^{1}J = 77.3, C$_1$), 37.55 (s, C$_6$), 41.20 (d, ^2J = 3.6, C$_5$), 61.66 (s, OCH$_2$), 121.0 (dd, ^1J = 82.7, ^2J = 13.7, C$_3$), 162.45 (dd, ^2J = 25.4, ^3J = 6.1, C$_4$), 167.58 (s, CO$_2$); mass spectrum m/z (rel intensity) 550 (M$^+$, 75), 503 (M$^+$ – SMe, 100). Anal. Calcd for $C_{22}H_{32}O_4P_2S_4$: C, 47.98; H, 5.86; P, 11.25; S, 23.29. Found: C, 47.73; H, 5.95; P, 10.96; S, 23.31.

3,3′,4,4′-Tetramethyl-6,6′-bis(ethoxycarbonyl)-2,2′-biphosphinine (16). A mixture of 2.0 g (3.6 × 10^{-3} mol) of the bis homophosphole sulfide 15 and 2.4 g (1.44 g × 10^{-2} mol) of triethyl phosphite was heated for 20 h at 150 °C. After cooling, the residue was twice chromatographed with toluene, leading to 0.85 g of a mixture of two products: the biphosphinine **16**, δ ^{31}P (CH$_2$Cl$_2$) 202.9, and the homophosphole–phosphinine **17**, δ ^{31}P (CH$_2$Cl$_2$) 207.7 (d) and 41.8 (d), $^3J_{PP}$ = 7.3 Hz. This mixture was once more chromatographed with toluene, giving first 0.3 g (yield 21.5%) of the biphosphinine 16 [^{31}P NMR (CDCl$_3$) δ 202.6; ^{1}H NMR (CDCl$_3$) δ 1.40 (t, $^3J_{HH}$ = 7.1, 6 H, CH$_3$), 2.12 (s, 6 H, C$_3$-CH$_3$), 2.50 (s, 6 H, C$_4$-CH$_3$), 4.41 (q, $^3J_{HH}$ = 7.1, 4 H, OCH$_2$), 8.45 (s, 2 H, C$_5$-H); ^{13}C NMR (CDCl$_3$) δ 14.35 (s, CH$_3$), 16.61 (s, C$_3$-CH$_3$), 23.35 (s, C$_4$-CH$_3$), 61.47 (s, OCH$_2$), 138.54 (pseudo t, C$_5$), 140.42 (pseudo t, C$_3$), 144.97 (s, C$_4$), 153.90 (AXX′, ^1J = 53.5, C$_6$), 168.10 (pseudo t, C$_2$), 172.10 (AXX′, ^2J = 21.4, CO$_2$); mass spectrum m/z (rel intensity) 390 (M$^+$, 100). Anal. Calcd for $C_{20}H_{24}O_4P_2$: C, 61.54; H, 6.20; P, 15.87. Found: C, 61.80; H, 6.39; P, 15.55.] and then 0.2 g of a mixture of about 30% of the biphosphinine 16 and 70% of the compound 17 [^{1}H NMR (CDCl$_3$) δ 8.35 (d, ^3J = 4.3, 0.55 H, **17** C$_5$-H), 8.44 (s, 0.45 H, **16** C$_5$-H); mass spectrum m/z (rel intensity) 438 (**17** M$^+$, 70), 390 (**16** M$^+$, 100), 365 (**17** M$^+$ – CO$_2$Et, 90), 317 (**16** M$^+$ – CO$_2$Et, 30)].

Supplementary Material Available: Structural report for 7, including a description of data collection, atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

Nickel-Catalyzed Olefination of Cyclic Benzylic Dithioacetals by Grignard Reagents. Scope and Mechanism[1]

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The details of the first nickel-catalyzed olefination of cyclic dithioacetals to form substituted styrenes and aryl-substituted 1,4-pentadienes are described. The reaction represents a new synthetic use of the dithioacetal functionality. Only nickel complexes catalyzed these cross-coupling reactions; palladium complexes displayed no catalytic activity under the reaction conditions employed. Selective coupling occurred. A mechanism for the reaction is proposed. The experimental evidence indicates that, in these nickel-catalyzed couplings, cyclic dithioacetals are more reactive than their acyclic analogues. This increased reactivity appears to be the result of maintaining the two sulfur atoms in close proximity to each other by the use of a short chain of methylene groups.

The dithioacetal functionality was first described in 1885.[3] Since that time it has come to be considered a latent carbonyl or methylene group.[4,5] However, reports of the transformation of the dithioacetal functionality to other functional groups have been few.[6–8] In general, the dithioacetal functionality is relatively stable toward nu-

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[1] Transition Metal Promoted Reactions. 33.

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Table I. Effect of Catalyst on the Coupling of 1 with MeMgI at Room Temperature

entry	catalyst	mol %	reactn time, h	yield (%)
1	$NiCl_2(PPh_3)_2$	6	18	70
2	$NiBr_2$·DME[a]	6	16	68
3	$NiCl_2$(dppe)	4	60	37
4	$NiCl_2$(dppp)	5	60	51
5	$Pd(PPh_3)_4$	4	16	0[b]
6	$PdCl_2(PPh_3)_2$	8	16	0[b]

[a] Ph_3P (12 mol %) was also present. [b] The reaction was carried out under reflux.

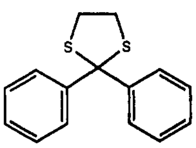
cleophiles. In a few cases, nucleophilic attack has led to carbon–carbon bond formation.[7] More recently, carbonyls of group 6 metals have been shown to convert dithioacetals to yield dimeric olefins.[8] Sulfur-containing organometallic complexes have been obtained from the reaction of dithioacetals and certain metal carbonyls.[9]

Several nickel complexes are highly thiophilic. The conversion of a C–S bond to a C–H bond[10,11] or to a C–C bond[10,12] induced by homogeneous nickel catalysts is well-documented. Examples of the latter include the coupling of allylic, aryl, and vinylic mercaptans, thioethers, and sulfones. However, benzyl methyl sulfide gave diphenylmethane in less than 9% yield upon treatment with PhMgBr in the presence of various catalysts,[13] and simple aliphatic thioethers were unreactive under various conditions.[12b]

Benzylic dithiolanes and dithianes possess two carbon–sulfur bonds. The ease with which such carbon–sulfur bonds are cleaved appears to be greater than that of the carbon–sulfur bond of simple benzylic thioethers. Furthermore, the close proximity of the two sulfur atoms to each other apparently plays a part in the facile cleavage of both carbon–sulfur bonds during these nickel-catalyzed reactions. One carbon–sulfur bond is broken and is replaced by a carbon–carbon bond, whereas the other is broken followed by a β-elimination which produces an olefin. This paper describes the scope and mechanism of the nickel-catalyzed olefination of cyclic benzylic dithioacetals.[14]

Results and Discussion

The Effect of the Catalyst. The reaction of 2,2-diphenyl-1,3-dithiolane (1) with MeMgI was examined in detail. For example, treatment of 1 at room temperature with MeMgI in the presence of catalytic amounts of $NiBr_2$·DME and Ph_3P gave 1,1-diphenylethene (**2a**) in 68% yield (Table I, entry 2). The use of 3 equiv of the Grignard reagent was necessary to force the reaction to completion. Table I shows the effect of the catalyst on the product yield. The most effective catalyst was $NiCl_2(PPh_3)_2$. This compound is less hygroscopic and easier to handle than $NiBr_2$·DME. Nickel catalysts that bear bidentate phosphine ligands like $Ph_2P(CH_2)_2PPh_2$(dppe) or $Ph_2P(CH_2)_3PPh_2$(dppp) were also effective, but more drastic conditions were required for reaction to occur (entries 3 and 4).[15] However, $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ were ineffective catalysts (entries 5 and 6). No reaction of 1 and Grignard reagents occurred in the absence of a nickel catalyst. It should be noted that benzylic acetals and Grignard reagents do react in the absence of a transition-metal catalyst to give alkylated ethers.[16]



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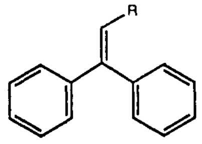
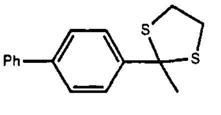
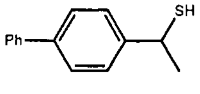


2 a R = H
b R = Me
c R = Pr

The Effect of the Nucleophile. Grignard reagents of various types reacted with cyclic dithioacetals under the reaction conditions employed. For example, when 1 was treated with EtMgBr or BuMgBr, the corresponding coupling product, **2b** or **2c**, was obtained in good yield. Alkyllithiums also react with dithiolanes to give mercaptans.[6a] Under our reaction conditions, this reaction competed with cross coupling. Thus, the reaction of **3a** with methyllithium gave a mixture of mercaptan **4** and olefin **5** in yields of 43% and 31%, respectively. However, when six-membered cyclic dithianes were employed, coupling with organolithium reagents went smoothly. Organozinc and organotin reagents failed to react with 1.



3a



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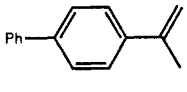

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Olefination of Cyclic Benzylic Dithioacetals. The presence of two aryl groups in the dithioacetal was not necessary for coupling to occur. Dithioacetals **6** of benzylic aldehydes afforded the corresponding styrenes **7** in good yields. The results of the nickel-catalyzed olefination of various dithioacetals are summarized in Table II. Thus,

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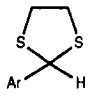

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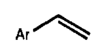

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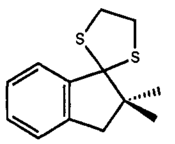

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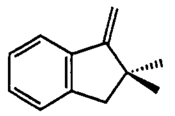
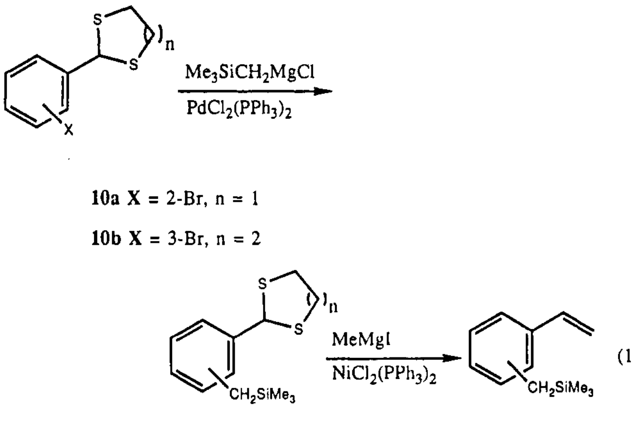


9

1,4-divinylbenzene (**7e**) was synthesized by this procedure (entry 11). An aryl ether linkage (entry 10)[17] remained intact under the reaction conditions. Although the C–S bond of thiophene can be cleaved under similar reaction conditions,[18,19] it apparently is cleaved less readily than the C–S bond of cyclic dithioacetals. Thus, **7f** was isolated from the reaction of **6f** in moderate yield (entry 12). The scope of the reaction could be extended to include sterically hindered dithioacetals. Thus, **8** gave the olefin **9**, which possesses an exocyclic carbon–carbon double bond, in 78% yield.

Aryl halides are reactive under the conditions employed.[14,20] Both nickel and palladium compounds catalyze the coupling of aryl halides with Grignard reagents.[20] As mentioned earlier, neither Pd(0) nor Pd(II) complexes catalyze the reaction of dithioacetals with Grignard reagents. Consequently, a chemoselective reaction could be achieved when both halide and dithioacetal functionalities were present. Equation 1 illustrates the application of this strategy to the synthesis of substituted styrenes.[21]



(1)

10a X = 2-Br, n = 1

10b X = 3-Br, n = 2

11a (n = 1) 98%

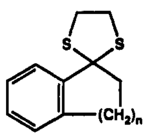
11b (n = 2) 99%

12a 86%

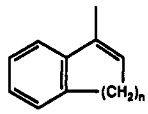
12b 84%

The dithioketals of cyclic ketones reacted to give olefins possessing endocyclic carbon–carbon double bonds as the sole products. For example, 3-methyl-1*H*-indene (**14a**) and 4-methyl-1,2-dihydronaphthalene (**14b**) were obtained, in 69% and 60% yield, respectively, from **13a** and **13b**.

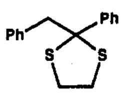
Cyclic dithioketals of methyl aryl ketones also reacted smoothly with MeMgI under the reaction conditions to give α-methylstyrenes. For example, **3a** and MeMgI reacted at room temperature to afford **5** in 95% yield.



13a n = 1
b n = 2



14a n = 1
b n = 2



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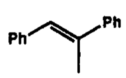

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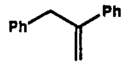

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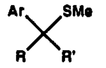
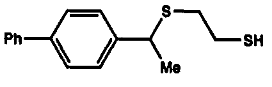


21a Ar = 4-PhC_6H_4, R = Me, R' = H
21b Ar = R = Ph, R' = Me



22

When dithioketal **15** was allowed to react with MeMgI, a 2:1 mixture of the isomers **16** and **17** was obtained in 94% yield. This result provided further evidence in support of the belief that the carbon–carbon bond was formed prior to the β-elimination, and the β-elimination was not selective. Thus, a mixture of isomeric olefins was produced.

The Mechanism of the Reaction. A plausible catalytic pathway for the olefination of dithioacetals, which is based on the general catalytic cycle[12,20] proposed for the coupling of aryl halides or sulfides with Grignard reagents, is outlined in Scheme I. The nickel(II) catalyst is first reduced to nickel(0) by the Grignard reagent. Evidence for this step was provided by the observation that, when MeMgI and Me_3SiCH_2MgCl were treated with a stoichiometric amount of $NiCl_2(PPh_3)_2$, ethane and $Me_3SiCH_2CH_2SiMe_3$ were detected by GC–MS. Then the two carbon–sulfur bonds of the dithioacetal are cleaved in succession. Thus, the oxidative addition of Ni(0) to the first carbon–sulfur bond produces the sulfur-coordinated intermediate **18**. In the next step, the alkyl group of the Grignard reagent may associate with nickel, followed by reductive elimination, to give the corresponding alkylated intermediate **19**.

That intermediate **19** is indeed formed was not confirmed. Attempts to detect **19** in the reaction mixture containing **1**, MeMgI, and various amounts of $NiCl_2(PPh_3)_2$ were unsuccessful. The reaction of **1** with 1.5 equiv of MeMgI under the usual conditions gave only **2a** and recovered starting material. These results implied that the rate of cleavage of the second carbon–sulfur bond was faster than that of the first carbon–sulfur bond. As mentioned earlier, benzylic thioether gave poor yields of coupling products.[13] It was also found that all of the benzylic thioether **21a** was recovered after attempted reaction with Grignard reagents at room temperature. Even the more reactive **2b** under reflux gave olefin **2a** in only 41% yield. No coupling product was obtained. It should be noted that the sulfide anion moiety in **19** is capable of coordination with the nickel species. Such coordination would facilitate the subsequent oxidative addition step, which leads to the cleavage of the second carbon–sulfur bond.

To test this hypothesis, sulfide **22**, which was synthesized by the partial reduction of dithiolane **3a** with tri-*n*-butyltin hydride,[23] was allowed to react with MeMgI in the presence of $NiCl_2(PPh_3)_2$ at room temperature. The reaction gave olefin **7g** in 61% yield. This result suggested that the coordination of the sulfide anion with the nickel atom did indeed assist in the cleavage of the carbon–sulfur bond of **19**. Thus, in the nickel-catalyzed coupling reactions of cyclic dithioacetals and Grignard reagents, *the tandem cleavage of the two carbon–sulfur bonds occurs rapidly. The nickel-catalyzed intermolecular cleavage of the first*

---

(17) The C–O bond of aryl methyl ethers can be cleaved under similar conditions. See: Wenkert, E.; Michelotti, E. L.; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2246.

(18) Wenkert, E.; Leftin, M. H.; Michelotti, E. L. *J. Chem. Soc., Chem. Commun.* **1984**, 617.

(19) Tiecco, M.; Tingoli, M.; Wenkert, E. *J. Org. Chem.* **1985**, *50*, 3828.

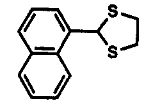
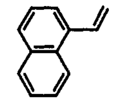
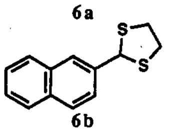
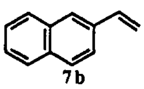
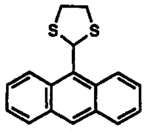
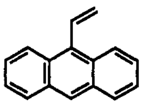
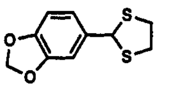
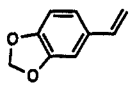
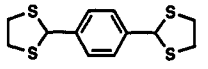
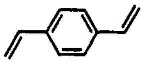
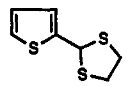
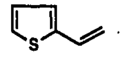
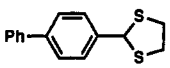
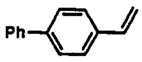
(20) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669.

(21) The related sequential cross coupling has been used extensively for the synthesis of olefins. See: Naso, F. *Pure Appl. Chem.* **1988**, *60*, 79.

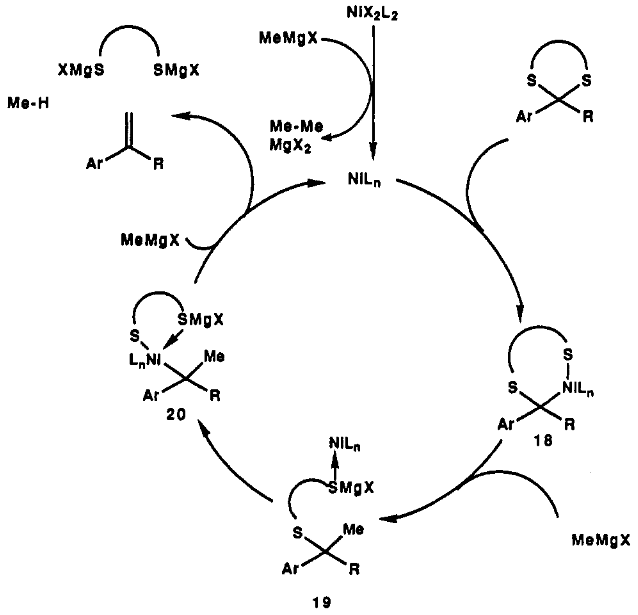
(22) (a) Wenkert, E.; Shepard, M. E.; McPhail, A. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1390. (b) Osakada, K.; Maeda, M.; Nakamura, Y.; Yamamoto, T.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1986**, 442.

(23) Gutierrez, C. G.; Stringham, R. A.; Nitasaka, T.; Glasscock, K. G. *J. Org. Chem.* **1980**, *45*, 3393.

Table II. Preparation of Styrenes by the Reaction of Cyclic Dithioacetals 6 with MeMgI in the Presence of NiCl$_2$(PPh$_3$)$_2$

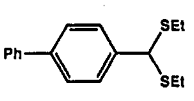
entry	dithioacetal	product	yield, %
7	 6a	 7a	83
8	 6b	 7b	94
9	 6c	 7c	88
10	 6d	 7d	71
11	 6e	 7e	58
12	 6f	 7f	62
13	 6g	 7g	93

Scheme I

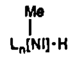


carbon–sulfur bond yields a product that promotes a subsequent intramolecular oxidative addition of the nickel species to the second carbon–sulfur bond. Thus, it was not surprising that the acyclic dithioacetal **23** proved to be much less reactive than the acyclic dithioacetals **6g**.[24]

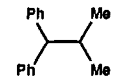
Cleavage of the second carbon–sulfur bond would give the sterically crowded alkylnickel intermediate **20**. Then β-elimination of a sulfur-containing nickel complex would give an olefin. Alternatively, the Grignard reagent may attack **20**. Subsequent β-elimination would then yield an olefin and intermediate **24**. If the latter reaction took place, the hydrocarbon derived from the Grignard reagent would be expected to be formed by subsequent reductive elimination from **24**. The active nickel(0) catalyst would thus be regenerated.



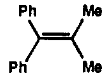
23



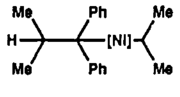
24



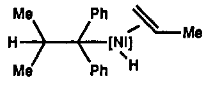
25



26



27



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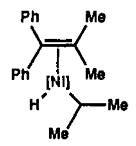
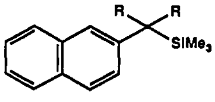


29

Several pieces of evidence support the conjecture that the Grignard reagent attacks **20** before β-elimination takes place. When Me$_3$SiCH$_2$MgCl was allowed to react with **1** under the usual conditions, Me$_4$Si was detected by GC–MS. Furthermore, reductive elimination could competitively give a dialkylated side product, for geminal dialkylation was observed in NiCl$_2$(dppe)-catalyzed reactions.[15] However, the data in Tables I and II show the absence of dimethylated products from the reactions of cyclic benzylic dithioacetals in the presence of NiCl$_2$(PPh$_3$)$_2$ catalyst. These results indicate that the β-elimination occurred rapidly.

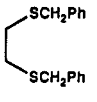
The results of the reaction of dithioacetal **1** with a secondary Grignard reagent are worth noting. When **1** was treated at room temperature with *i*-PrMgBr, a 6.7:1 mixture of 1,1-diphenyl-2-methylpropane (**25**) and 1,1-diphenyl-2-methylpropene (**26**) was produced. This result was somewhat different from those of the reactions of **1** with straight-chain Grignard reagents, which yielded no reduction products. The formation of **26** is consistent with the mechanism shown in Scheme I. Apparently, intermediate **27** can undergo β-hydride elimination involving either the secondary alkyl group or the 1,1-diphenyl-2-methylpropyl group to give nickel hydride **28** or **29**, respectively. Reductive elimination of a nickel species from **28** would give **25**.

Similarly, when the highly sterically hindered dithioketal **30a** was treated with EtMgBr under the usual conditions, the reduction product **30b** was obtained exclusively, in 56% yield. Again, steric congestion in the reaction intermediate would favor β-elimination involving the ethyl group. Reductive elimination would furnish the reduction product. These results clearly indicated that some sort of interaction between the Grignard reagent and **20** prior to β-elimination was essential.



30a R-R = -S(CH$_2$)$_3$S-

30b R = H



31

The fate of the sulfur moiety in these coupling reactions has been determined. Thus, to a reaction mixture of **1** and MeMgI under the usual conditions were added in suc-

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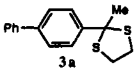
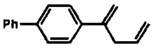
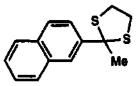
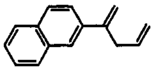
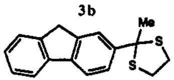
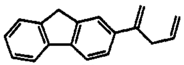
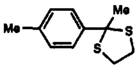
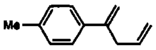
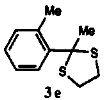
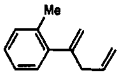
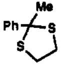
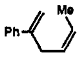
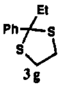
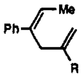
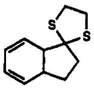
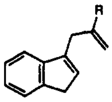
(24) Stilbene and sulfur-containing dimers were occasionally obtained as side products when more vigorous conditions (e.g., refluxing benzene) were employed. See: Ni, Z.-J. Ph.D. Dissertation, The Chinese University of Hong Kong, 1989.

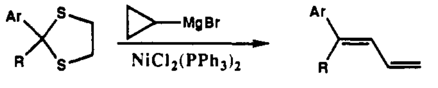
Table III. Preparation of 2-Aryl-1,4-pentadienes by the Reaction of Cyclic Dithioketals 3 with Allylmagnesium Halides in the Presence of the Nickel Catalyst

entry	dithioketals	Grignard reagent[a]	catalyst		product (% yield)
14	 3a	A	$NiCl_2(dppe)$	 32a	(73)
15	 3b	A	$NiCl_2(dppe)$	 32b	(77)
16	 3c	A	$NiCl_2(dppe)$	 32c	(65)
17	 3d	A	$NiCl_2(PPh_3)_2$	 32d	(82)
18	 3e	A	$NiCl_2(PPh_3)_2$	 32e	(67)[b]
19	 3f	B	$NiCl_2(dppe)$	 32f	(73)
20	 3g	A	$NiCl_2(dppe)$		32g R=H (71)
21		C			32h R = Me (62)
22	 13a	A	$NiCl_2(dppe)$		32i R=H (86)
23		C			32j R = Me (74)

[a] A, $CH_2{=}CHCH_2MgBr$; B, $MeCH{=}CHCH_2MgCl$; C, $CH_2{=}C(Me)CH_2MgCl$. [b] 33 was obtained in 15% yield.

cession aqueous NaOH and excess benzyl bromide. Workup gave the bisthioether 31 in 47% yield.

1,4-Pentadienes. It was recently shown that a cyclopropyl Grignard reagent could act as an allyl anion synthon in nickel-catalyzed cross couplings with dithioacetals (eq 2).[14c] A comparison of the behavior of the allyl Grignard

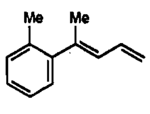


(2)

reagent and that of its cyclopropyl analogue proved informative. Hence, when a benzene solution of each of the dithioacetals 3 was refluxed with an allylmagnesium bromide in the presence of 5 mol % of either $NiCl_2(dppe)$ or $NiCl_2(PPh_3)_2$, the corresponding 1,4-pentadiene (32) was produced (Table III).

Similar results were obtained from the reactions of methallyl and crotyl Grignard reagents (entries 19, 21, and 23). It was noteworthy that the reaction of crotylmagnesium chloride gave regio- and stereoselectively a single isomer (entry 19). The assignment of stereochemistry to **32f** was based on an NOE experiment. The results were somewhat different from those of the coupling of vinyl triflates with crotyl cuprates, from which a mixture of regio- and stereoisomers was obtained.[25] It is interesting to note that the reaction of the dithioketal of phenyl ethyl ketone stereospecifically yielded only one isomer (entries 20 and 21).

The regioselective formation of 1,4-dienes from dithioacetals is mechanistically interesting and synthetically useful. Presumably, the steric environment of the transition states (**34** and **35**) of the β-elimination step determines which diene is formed.[26] β-elimination via **34** seems to have been favored. However, the degree of selectivity decreased with an increase in the degree of steric congestion in the dithioacetal. Hence, **3e**, in which an ortho methyl group was present on the aromatic ring, gave a significant amount of **33** (entry 18).



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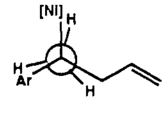

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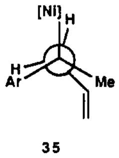

35

Experimental Section

General. Melting and boiling points are uncorrected. Schlenk techniques were used to manipulate air-sensitive compounds.[27a] All solvents were purified by standard methods.[27b] Tetrahydrofuran was distilled from sodium benzophenone ketyl. Benzene was distilled from sodium wire. Et_2O was refluxed over and distilled from $LiAlH_4$. $NiCl_2(PPh_3)_2$,[28] $NiCl_2(dppe)$,[29] $NiCl_2(dppp)$,[29] $PdCl_2(PPh_3)_2$,[30] and $Pd(PPh_3)_4$[31] were prepared by literature methods.

Reaction of 2,2-Diphenyl-1,3-dithiolane (1) with MeMgI Catalyzed by $NiBr_2$·DME and Ph_3P. Dithioketal 1 (246 mg, 0.95 mmol), $NiBr_2$·DME (15 mg, 0.06 mmol), and Ph_3P (30 mg, 0.11 mmol) were mixed under an atmosphere of dry N_2. Benzene (5 mL) was introduced by syringe, and the mixture was immersed in an ice bath. To the stirred mixture was then added, in one portion, by syringe, MeMgI (3 mL, 1.0 M in ether, 3 mmol). The mixture was stirred at room temperature for 16 h. Then it was quenched with saturated aqueous NH_4Cl (20 mL). The two liquid layers were separated. The aqueous layer was then extracted with Et_2O (2 × 30 mL). The combined organic layers were washed with 10% aqueous NaOH (2 × 10 mL) and water and were dried (Na_2SO_4). The solvent was evaporated from the filtrate in vacuo. The residue was purified by column chromatography on silica gel (hexane) to give **2a**[32] as a colorless oil (126 mg, 68%): IR (neat) ν 3050, 3025, 1653, 1597, 1440, 1317, 1275, 1021, 900, 770, 698 cm^{-1}; ^1H NMR (60 MHz) δ 5.35 (s, 2 H), 7.20 (s, 10 H); MS m/z (relative intensity) 180 (M^+, 23.3), 77 (base peak).

General Procedure for the Nickel-Catalyzed Coupling of Dithioacetal with "Simple" Alkyl Grignard Reagents. To an ice-cold stirred mixture of the dithioacetal, a catalytic amount (5–10 mol %) of $NiCl_2(PPh_3)_2$, and benzene was added the Grignard reagent (3–4 equiv, in Et_2O). The mixture was then stirred at room temperature until it was quenched with saturated aqueous NH_4Cl. The two liquid layers were separated. The aqueous portion was extracted with Et_2O. The combined organic layers were washed with 10% aqueous NaOH and water and were dried (Na_2SO_4). After the solvent was evaporated from the filtrate in vacuo, the residue was purified by column chromatography on silica gel (hexane, unless otherwise specified) to give the olefin.

$NiCl_2(PPh_3)_2$-Catalyzed Reaction of 1 with MeMgI. In a manner similar to that described in the general procedure, a mixture of 1 (253 mg, 0.98 mmol), $NiCl_2(PPh_3)_2$ (42 mg, 0.06 mmol), and MeMgI (3 mL of a 1 M solution in Et_2O, 3 mmol) in benzene (5 mL) was stirred at room temperature for 18 h to give **2a** (124 mg, 70%).

$NiCl_2(dppe)$-Catalyzed Reaction of 1 with MeMgI. In a manner similar to that described in the general procedure, a

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mixture of 1 (288 mg, 1.1 mmol) and $NiCl_2$(dppe) (25 mg, 0.04 mmol) in benzene (5 mL) was allowed to react with MeMgI (3 mL of a 1 M solution in Et_2O, 3 mmol) at room temperature to afford **2a** (74 mg, 37%).

$NiCl_2$(dppp)-Catalyzed Reaction of 1 with MeMgI. In a manner similar to that described in the general procedure, a mixture of 1 (250 mg, 0.97 mmol) and $NiCl_2$(dppp) in benzene (5 mL) was allowed to react with MeMgI (3 mL of a 1 M solution in Et_2O, 3 mmol) at room temperature to afford **2a** (89 mg, 51%).

Attempted Palladium-Catalyzed Reaction of 1 with MeMgI. To a benzene solution (2 mL) of 1 (121 mg, 0.47 mmol) and $PdCl_2(PPh_3)_2$ (25 mg, 0.036) was added MeMgI (2 mL of a 1 M solution in Et_2O, 2 mmol). The yellow solution immediately became colorless. The reaction was monitored by TLC. After stirring for 16 h, no sign of reaction was detected. The mixture was then heated under reflux for 20 h. TLC analysis again showed that no reaction had occurred. After the usual workup, 1 was recovered (87 mg, 72%).

From a similar attempt, in which $Pd(PPh_3)_4$ was used as the catalyst, 1 was recovered in 85% yield.

1,1-Diphenylpropene (2b). In a manner similar to that described in the general procedure, a mixture of 1 (243 mg, 0.94 mmol), $NiCl_2(PPh_3)_2$ (33 mg, 0.05 mmol), EtMgBr (3 mL of a 1 M solution in Et_2O, 3 mmol), and benzene (5 mL) was stirred at room temperature for 15 h to afford **2b**[33] (143 mg, 78%): IR (neat) 3050, 3020, 2900, 1650, 1592, 1490, 1438, 1270, 1063, 1023, 918, 838, 750, 695 cm^{-1}; ^{1}H NMR (60 MHz) δ 1.69 (d, J = 7 Hz, 3 H), 6.08 (q, J = 7 Hz, 1 H), 6.91–7.63 (m, 10 H); MS m/z (relative intensity) 195 ($M^+ + 1$, 16.5), 194 (M^+, 100.0), 193 (58.8), 179 (30.6), 117 (16.2), 91 (16.7).

1,1-Diphenylpentene (2c). In a manner similar to that described in the general procedure, a mixture of 1 (252 mg, 0.98 mmol), $NiCl_2(PPh_3)_2$ (49 mg, 0.07 mmol), and benzene (5 mL) was allowed to react with n-BuMgBr (3 mL of a 1 M solution in Et_2O, 3 mmol) at room temperature for 16 h to give **2c**[34] (183 mg, 84%): IR (neat) ν 3051, 2931, 1650, 1597, 1495, 1440, 1310, 1270, 940, 920, 741, 700 cm^{-1}; ^{1}H NMR (60 MHz) δ 0.88 (t, J = 7 Hz, 3 H), 1.07–1.93 (m, 2 H), 2.07 (dt, J = 7.5 Hz, J = 5 Hz, 2 H), 6.05 (t, J = 7.5 Hz, 1 H), 6.95–7.65 (m, 10 H); MS m/z (relative intensity) 223 ($M^+ + 1$, 8.8), 222 (M^+, 46.7), 193 (100.0), 178 (23.5), 165 (15.8), 115 (67.9), 91 (32.7).

Reaction of 2-Methyl-2-(4-biphenylyl)-1,3-dithiolane (3a) with MeLi Catalyzed by $NiCl_2(PPh_3)_2$. To a stirred solution of **3a** (95 mg, 0.35 mmol), $NiCl_2(PPh_3)_2$ (22 mg, 0.034 mmol), and benzene (3 mL) was added MeLi (10 mL of a 0.2 M solution in Et_2O, 2 mmol) under a N_2 atmosphere. The mixture was refluxed for 16 h and was then cooled to room temperature, and water (30 mL) was added. The aqueous layer was extracted with Et_2O (2 × 30 mL). The combined organic layers were washed twice with water and dried (Na_2SO_4). Evaporation of the solvent gave a solid. This was purified by column chromatography on silica gel (hexane) to afford 1-(4-biphenylyl)ethanethiol (4) (32 mg, 43%) and 2-(4-biphenylyl)propene (5) (21 mg, 31%). **4**: IR (neat) ν 3051, 3009, 2911, 1595, 1481, 1445, 1422, 1380, 1270, 1155, 1102, 901, 842, 723 cm^{-1}; ^{1}H NMR (60 MHz) δ 1.68 (d, J = 7 Hz, 3 H), 2.02 (d, J = 5 Hz, 1 H), 4.0–4.51 (m, 1 H), 7.03–7.90 (m, 9 H); exact mass calcd for $C_{14}H_{14}S$ 214.0816, found 214.0813. **5**: mp 117–118 °C (lit.[35] mp 119–119.5 °C); IR (KBr) ν 3040, 2980, 2930, 1688, 1627, 1585, 1489, 1411, 1005, 837, 841, 770, 737, 690 cm^{-1}; ^{1}H NMR (200 MHz) δ 2.11 (s, 3 H), 5.05 (d, J = 0.2 Hz, 1 H), 5.36 (d, J = 0.2 Hz, 1 H), 7.25–7.51 (m, 9 H); ^{13}C NMR (50 MHz) δ 21.2, 125.9, 126.9, 127.0, 127.3, 128.8, 140.1, 140.2, 140.8, 142.8; exact mass calcd for $C_{15}H_{14}$ 194.1096, found 194.1100.

General Procedure for the Synthesis of Styrenes 7. To a solution of dithioacetal **3** (1 mmol), $NiCl_2(PPh_3)_2$ (0.05 mmol), and benzene (10 mL) was added, in one portion, MeMgI (10 mL of a 0.3 M solution in Et_2O, 3 mmol). The mixture was refluxed for 16 h. The mixture was then poured into saturated aqueous NH_4Cl and was extracted with Et_2O (2 × 20 mL). The combined extracts were washed sequentially with 10% aqueous NaOH (2 × 20 mL) and water (2 × 20 mL) and were dried ($MgSO_4$). The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel (hexane) to afford the corresponding styrene.

2-[(Trimethylsilyl)methyl]styrene (12a): IR (neat) ν 3069, 3027, 2960, 2900, 1628, 1603, 1483, 1451, 1419, 1253, 1215, 1188, 1156, 1048, 990, 910, 850, 768, 692 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.03 (s, 9 H), 2.22 (s, 2 H) 5.27 (d, J = 11.0 Hz, 1 H), 5.64 (d, J = 17.0 Hz, 1 H), 6.88–7.17 (m, 4 H), 7.48–7.52 (m, 1 H); MS m/z 190. Anal. Calcd for $C_{12}H_{18}Si$: C, 75.72; H, 9.53. Found: C, 75.33; H, 9.15.

3-[(Trimethylsilyl)methyl]styrene (12b):[36] IR (neat) ν 3060, 3040, 2960, 2900, 1632, 1600, 1580, 1485, 1416, 1250, 1162, 1078, 990, 905, 890, 800, 695 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.03 (s, 9 H), 2.11 (s, 2 H), 5.24 (d, J = 11.0 Hz, 1 H), 5.75 (d, J = 17.0 Hz, 1 H), 6.71 (dd, J = 11.0, 17.0 Hz, 1 H), 6.91–7.24 (m, 4 H); MS m/z 190. Anal. Calcd for $C_{12}H_{18}Si$: C, 75.72; H, 9.53. Found: C, 75.57; H, 9.10.

2-[2-[(Trimethylsilyl)methyl]phenyl]dithiolane (11a). To a stirred solution of **10a** (780 mg, 2.99 mmol), $PdCl_2(PPh_3)_2$ (110 mg, 0.16 mmol), and benzene (20 mL) was added Me_3SiCH_2MgCl (20 mL of a 0.5 M solution in Et_2O, 10 mmol). The mixture was refluxed for 16 h. The mixture was then poured into saturated aqueous NH_4Cl and extracted with Et_2O (2 × 30 mL). The combined extracts were washed with water (2 × 30 mL) and were dried ($MgSO_4$). The solvent was evaporated in vacuo to afford **11a** (790 mg, 98%) as a yellow liquid. This was distilled to give **11a** as colorless liquid: bp 140 °C (0.4 mm); IR (neat) ν 3064, 3022, 2959, 1602, 1480, 1450, 1422, 1280, 1250, 1180, 1156, 842, 769, 741, 692 cm^{-1}; ^{1}H NMR δ −0.02 (s, 9 H), 2.16 (s, 2 H), 3.21–3.47 (m, 4 H), 5.72 (s, 1 H), 6.84–7.06 (m, 4 H); MS m/z 268. Anal. Calcd for $C_{13}H_{20}S_2Si$: C, 58.19; H, 7.52. Found: C, 57.75; H, 7.49.

2-[3-[(Trimethylsilyl)methyl]phenyl]dithiane (11b). A mixture of **10b** (830 mg, 3.02 mmol), $PdCl_2(PPh_3)_2$ (108 mg, 0.15 mmol), benzene (20 mL), and Me_3SiCH_2MgCl (20 mL of a 0.5 M solution in Et_2O, 10 mmol) was treated in the same manner as described above to give **11b** (839 mg, 99%): bp 155 °C (0.3 mm); IR (neat) ν 3060, 3030, 2959, 2900, 1664, 1601, 1485, 1280, 1250, 1160, 1074, 950, 894, 850, 762, 750, 700 cm^{-1}; ^{1}H NMR δ −0.01 (s, 9 H), 1.83–2.19 (m, 4 H), 2.85–3.18 (m, 4 H), 5.11 (s, 1 H), 6.90–7.24 (m, 4 H); MS m/z 282. Anal. Calcd for $C_{14}H_{22}S_2Si$: C, 59.52; H, 7.85. Found: C, 59.57; H, 7.70.

2,2-Dimethyl-1-methyleneindan (9). According to the general procedure described above, a mixture of **8** (251 mg, 1.06 mmol) and $NiCl_2(PPh_3)_2$ (59 mg, 0.09 mmol) in benzene (5 mL) was allowed to react with MeMgI (4.0 mL, 1 M in Et_2O, 4.0 mmol) under refluxing conditions for 16 h to give **9** as a colorless liquid (131 mg, 78%): IR (neat) ν 3034, 2862, 1631, 1584, 1324, 1161, 1005, 886, 771, 723 cm^{-1}; ^{1}H NMR (250 MHz) δ 1.22 (s, 6 H), 2.82 (s, 2 H), 4.92 (s, 1 H), 5.44 (s, 1 H), 7.18–7.20 (m, 3 H), 7.45–7.49 (m, 1 H); ^{13}C NMR δ 29.4, 42.6, 47.1, 100.9, 121.1, 125.3, 126.5, 128.5, 140.4, 143.5, 160.1; exact mass calcd for $C_{12}H_{14}$ 158.1085, found 158.1080.

4-Methyl-1,2-dihydronaphthalene (14b). In a manner similar to that described in the general procedure, a mixture of **13b** (117 mg, 0.53 mmol), $NiCl_2(PPh_3)_2$ (35.2 mg, 0.054 mmol), MeMgI (2 mL of a 1 M solution in Et_2O, 2 mmol), and benzene (1 mL) was stirred at room temperature for 15 h to afford **14b**[37] (46 mg, 60%): IR (neat) ν 3035, 2950, 1582, 1239, 1204, 978 cm^{-1}; ^{1}H NMR (60 MHz) δ 1.93–2.93 (m, 7 H, br s at 2.01), 5.62–5.90 (m, 1 H), 7.00–7.30 (m, 4 H); MS m/z (relative intensity) 145 ($M^+ + 1$, 7.1), 144 (M^+, 55.0), 129 ($M - CH_3$, 100.0), 115 (14.7); exact mass calcd for $C_{11}H_{12}$ 144.0939, found 144.0946.

3-Methyl-1*H*-indene (14a). In a manner similar to that described in the general procedure, a mixture of **13a** (210 mg, 1.0 mmol), $NiCl_2(PPh_3)_2$ (30 mg, 0 05 mmol), MeMgI (4.0 mL of a 1 M solution in Et_2O, 4.0 mmol), and benzene (2 mL) was stirred at room temperature for 16 h to give **14a**[38] (90 mg, 69%): IR (neat) ν 3030, 2946, 1582, 1238, 978, 763 cm^{-1}; ^{1}H NMR (60 MHz) δ

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2.03–2.30 (br s, 3 H), 3.10–3.43 (br s, 2 H), 6.10 (br s, 1 H); 6.93–7.53 (m, 4 H); MS m/z (relative intensity) 131 (M$^+$ + 1, 14.1), 130 (M$^+$, 100.0), 115 (M − CH$_3$, 50.1), 77 (11.4).

2-(4-Biphenylyl)propene (5). In a manner similar to that described in the general procedure, a mixture of **3a** (266 mg, 0.98 mmol), NiCl$_2$(PPh$_3$)$_2$ (42 mg, 0.06 mmol), MeMgI (3 mL of a 1 M solution in Et$_2$O, 3 mmol), and benzene (5 mL) was heated under reflux for 18 h to give **5** (180 mg, 95%): mp 117–118 °C. The spectra of **5** were identical with those of an authentic sample.

General Procedure for the Reaction of 3 with Allylmagnesium Halides. To a solution of allyl Grignard reagent [freshly prepared from Mg (8 g-atom), allyl halide (8 mmol), and Et$_2$O (10 mL)] was added, under N$_2$, a solution of dithioacetal (1 mmol) and either NiCl$_2$(dppe) or NiCl$_2$(PPh$_3$)$_2$ (0.05 mmol) in benzene (8 mL) in one portion. The mixture was heated under reflux for 16 h. The cooled solution was then poured into saturated aqueous NH$_4$Cl and was extracted with Et$_2$O (2 × 20 mL). The combined extracts were washed sequentially with 10% aqueous NaOH (2 × 20 mL) and water (2 × 20 mL) and were dried (MgSO$_4$). The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel (hexane) to afford the corresponding 1,4-diene. An analytical sample was obtained by recrystallization, distillation, or preparative GC (6-ft SE30 column).

2-(4-Biphenylyl)-1,4-pentadiene (32a). In a manner similar to that described in the general procedure, a mixture of **3a** (272 mg, 1.0 mmol) and benzene (8 mL) was treated in the presence of NiCl$_2$(dppe) (32.7 mg, 0.05 mmol) with CH$_2$=CHCH$_2$MgBr (8 mmol) to give **32a** (101 mg, 73%): mp 43–45 °C; IR (neat), ν 3029, 2925, 1637, 1601, 1485, 1446, 843, 770, 740, 697 cm^{-1}; ^{1}H NMR δ 3.28 (d, J = 6.0 Hz, 2 H), 5.05–5.19 (m, 3 H), 5.46 (br s, 1 H), 5.80–6.05 (m, 1 H), 7.35–7.60 (m, 9 H); ^{13}C NMR δ 39.4, 113.2, 116.5, 126.9, 127.2, 128.7, 136.2, 139.7, 140.2, 140.6, 145.7; exact mass calcd for C$_{17}$H$_{16}$ 220.1252, found 220.1254.

2-(2-Naphthyl)-1,4-pentadiene (32b). In a manner similar to that described in the general procedure in which NiCl$_2$(dppe) was the catalyst, **3b** (246 mg, 1.0 mmol) was converted to **32b** (149 mg, 77%): an oil; IR (neat) ν 3034, 2925, 803, 779 cm^{-1}; ^{1}H NMR δ 3.22 (d, J = 5.8 Hz, 2 H), 5.05–5.14 (m, 3 H), 5.42 (br s, 1 H), 5.75–6.00 (m, 1 H), 7.25–8.04 (m, 7 H); ^{13}C NMR δ 30.8, 42.8, 115.9, 116.5, 125.0, 125.1, 125.6, 127.2, 128.2, 131.1, 133.7, 135.6; exact mass calcd for C$_{15}$H$_{14}$ 194.1095, found 194.1088.

2-(2-Fluorenyl)-1,4-pentadiene (32c). In a manner similar to that described in the general procedure in which NiCl$_2$(dppe) was the catalyst, **3c** (284 mg, 1.0 mmol) was converted to **32c** (151 mg, 65%): mp 55–57 °C; IR (neat) ν 3056, 2966, 1613, 1456, 1263, 802, 740 cm^{-1}; ^{1}H NMR 3.32 (d, J = 6.6 Hz, 2 H), 3.88 (s, 2 H), 5.09–5.19 (m, 3 H), 5.45 (br s, 1 H), 5.84–6.04 (m, 1 H), 7.25–7.85 (m, 7 H); ^{13}C NMR δ 36.9, 76.4, 112.8, 116.4, 119.5, 119.9, 122.6, 124.8, 124.9, 126.6, 126.7, 136.3, 139.5, 141.1, 141.4, 143.3, 143.4, 146.5; exact mass calcd for C$_{18}$H$_{14}$ 232.1252, found 232.1255.

2-(4-Tolyl)-1,4-pentadiene (32d). In a manner similar to that described in the general procedure, **3d** (210 mg, 1 mmol) was allowed to react in the presence of NiCl$_2$(PPh$_3$)$_2$ (32.7 mg, 0.05 mmol) with CH$_2$=CHCH$_2$MgBr (8 mmol) to give **32d** (130 mg, 82%): IR (neat) ν 3081, 2978, 1624, 1512, 1433, 1121, 893, 824, 734; ^{1}H NMR δ 2.34 (s, 3 H), 3.24 (d, J = 6.4 Hz, 2 H), 5.05–5.15 (m, 3 H), 5.36 (br s, 1 H), 5.80–6.00 (m, 1 H), 7.13 (d, J = 8.0 Hz, 2 H), 7.33 (d, J = 8.0 Hz, 2 H); ^{13}C NMR δ 19.7, 39.5, 112.3, 116.3, 125.8, 128.9, 136.3, 137.2, 148.1.

2-(2-Tolyl)-1,4-pentadiene (32e). In a manner similar to that described in the general procedure, **3e** (210 mg, 1.0 mmol) was allowed to react in the presence of NiCl$_2$(PPh$_3$)$_2$ (32.7 mg, 0.05 mmol) with CH$_2$=CHCH$_2$MgBr (8 mmol) to give a 4:1 mixture of **32e** and 4-(2-tolyl)-1,3-pentadiene (**33e**)[14c] (128 mg, 82%). The two isomers were separated by preparative gas chromatography. **32e**: IR (neat) ν 3076, 2923, 1638, 1485, 1430, 909, 766, 730 cm^{-1}; ^{1}H NMR δ 2.29 (s, 3 H), 3.55 (d, J = 6.0 Hz, 2 H), 4.91–5.20 (m, 3 H), 5.73–5.94 (m, 1 H), 7.05–7.16 (m, 4 H); ^{13}C NMR δ 19.6, 42.0, 114.4, 116.4, 125.3, 126.6, 128.3, 130.0, 134.7, 135.6, 142.8, 148.3.

(*Z*)-Phenyl-1,4-hexadiene (32g). In a manner similar to that described in the general procedure, **3g** (198 mg, 1.0 mmol) was allowed to react in the presence of NiCl$_2$(dppe) (26.4 mg, 0.05 mmol) with CH$_2$=CHCH$_2$MgBr (8 mmol) to give **32g** (112 mg, 71%): ^{1}H NMR δ 1.60 (d J = 6.9 Hz, 3 H), 3.25 (d, J = 5.7 Hz, 2 H), 4.96–5.11 (m, 2 H), 5.76–5.98 (m, 1 H), 7.16–7.39 (m, 4 H); ^{13}C NMR δ 14.2, 34.1, 115.1, 124.2, 125.9, 126.4, 128.1, 135.6, 137.6; exact mass calcd for C$_{12}$H$_{14}$ 158.1095, found 158.1091.

3-Allyl-1*H*-indene (32i). In a manner similar to that described in the general procedure in which NiCl$_2$(dppe) was the catalyst, **13a** (208 mg, 1.0 mmol) was converted to **32i** (134 mg, 86%): IR (neat) ν 3052, 2920, 11455, 1089, 758 cm^{-1}; ^{1}H NMR δ 2.34–3.30 (m, 4 H), 5.13 (d, J = 10 Hz, 1 H), 5.19 (d, J = 18 Hz, 1 H), 5.94–6.14 (m, 1 H), 6.24 (s, 1 H), 7.10–7.55 (m, 4 H); ^{13}C NMR δ 32.4, 77.2, 116.2, 119.1, 123.7, 124.5, 125.9, 128.9, 135.6, 142.4, 144.5, 145.1; exact mass calcd for C$_{12}$H$_{12}$ 156.0939, found 156.0936.

2-Phenyl-1,4-hexadiene (32f). In a manner similar to that described in the general procedure, **3f** (196 mg, 1.0 mmol) was allowed to react in the presence of NiCl$_2$(dppe) (26.4 mg, 0.05 mmol) with MeCH=CHCH$_2$MgBr (8 mmol) to give **32f** (106 mg, 73%): ^{1}H NMR δ 1.86 (br s, 3 H), 3.20 (br s, 2 H, 4.4% NOE enhancement upon irradiation at δ 1.86), 5.08 (br s, 1 H), 5.34 (br s, 1 H), 5.53 (m, 2 H), 7.22–7.46 (m, 5 H); ^{13}C NMR δ 14.5, 17.9, 112.6, 125.9, 126.9, 127.3, 128.2, 128.6, 141.1, 147.1; exact mass calcd for C$_{12}$H$_{14}$ 158.1095, found 158.1099.

2-Methyl-4-phenyl-1,4-hexadiene (32h). In a manner similar to that described in the general procedure, **3g** (210 mg, 1.0 mmol) was allowed to react in the presence of NiCl$_2$(dppe) (26.4 mg, 0.05 mmol) with CH$_2$=C(Me)CH$_2$MgBr (8 mmol) to give **32h** (106 mg, 62%): ^{1}H NMR δ 1.76 (d, J = 8.0 Hz, 3 H), 1.79 (s, 3 H), 3.17 (br s, 2 H), 4.70 (br s, 1 H), 4.75 (br s, 1 H), 5.96 (q, J = 8.0 Hz, 1 H), 7.18–7.35 (m, 5 H); ^{13}C NMR δ 14.4, 22.9, 37.9, 110.8, 124.8, 125.9, 126.4, 128.1, 137.8, 142.8, 143.6; exact mass calcd for C$_{12}$H$_{14}$ 158.1095, found 158.1091.

3-Methallyl-1*H*-indene (32j). In a manner similar to that described in the general procedure, **13a** (208 mg, 1.0 mmol) was allowed to react in the presence of NiCl$_2$(dppe) (26.4 mg, 0.05 mmol) with CH$_2$=C(Me)CH$_2$MgBr (8 mmol) to give **32j** (126 mg, 74%): ^{1}H NMR δ 1.77 (s, 3 H), 3.29 (s, 2 H), 3.34 (s, 2 H), 4.82 (br s, 2 H), 6.24 (br s, 1 H), 7.15–7.24 (m, 4 H); ^{13}C NMR δ 36.9, 37.8, 112.2, 119.6, 123.7, 124.5, 126.0, 130.1, 141.9, 143.4, 144.6, 145.4; exact mass calcd for C$_{12}$H$_{14}$ 170.1095, found 170.1098.

Reaction of 2-Benzyl-2-phenyl-1,3-dithiolane (15) with MeMgI. In a manner similar to that described in the general procedure, a mixture of **15** (260 mg, 0.95 mmol), NiCl$_2$(PPh$_3$)$_2$ (32 mg, 0.05 mmol), MeMgI (3 mL of a 1 M solution in Et$_2$O, 3 mmol), and benzene (5 mL) was stirred at room temperature for 16 h to yield a 2:1 mixture of (*E*)-1,2-diphenylpropene (**16**) and 2,3-diphenylpropene (**17**, 173 mg, 94%). The **16**:**17** ratio was determined by ^{1}H NMR analysis. The two olefins were separated by preparative TLC (hexane). **16**:[39] IR (neat) ν 3052, 2951, 1599, 1496, 1442, 1361, 1072, 908, 753, 700 cm^{-1}; ^{1}H NMR (60 MHz) δ 2.20 (d, J = 2 Hz, 3 H), 6.75 (q, J = 2 Hz, 1 H), 7.03–7.56 (m, 10 H); MS m/z (relative intensity) 195 (M$^+$ + 1, 7.4), 194 (M$^+$, 100.0), 177 (25.3), 103 (10.6), 91 (7.0). **17**:[40] IR (neat) ν 3050, 2951, 1590, 1489, 1360, 1077, 755, 698 cm^{-1}; ^{1}H NMR (60 MHz) δ 3.77 (br s, 2 H), 4.95 (br s, 1 H), 5.42 (br s, 1 H), 7.04–7.55 (m, 10 H); MS m/z (relative intensity) 195 (M$^+$ + 1, 8.6), 194 (M$^+$, 100), 91 (67.3).

Reaction of 21a with MeMgI Catalyzed by NiCl$_2$(PPh$_3$)$_2$. MeMgI (3 mL of a 1 M solution in Et$_2$O, 3 mmol) was added to a solution of sulfide **21a** (45.4 mg, 0.20 mmol), NiCl$_2$(PPh$_3$)$_2$ (9.7 mg, 0.015 mmol), and benzene (2 mL). The mixture was refluxed for 3 days. After the usual workup, **21a** was recovered (42 mg, 93%).

Reaction of 2,2-Diphenyl-3-thiabutane (21b) with MeMgI Catalyzed by NiCl$_2$(PPh$_3$)$_2$. To a solution of **21b** (142 mg, 0.59 mmol), NiCl$_2$(PPh$_3$)$_2$ (20.4 mg, 0.03 mmol), and THF (5 mL) under N$_2$ was added MeMgI (2 mL, 2 mmol) via syringe. The mixture was refluxed for 16 h. After the usual workup (treatment with saturated aqueous NH$_4$Cl, extraction, washing with 10% aqueous NaOH) and chromatographic purification, **2a** was obtained (43 mg, 41%). Its spectra were identical with those of an authentic sample.

4-(4-Biphenylyl)-3-thiapentane-1-thiol (22). A mixture of **3a** (0.5 g, 1.84 mmol), tri-*n*-butyltin hydride (0.7 g, 2.41 mmol), and dibenzoyl peroxide (10 mg, 0.04 mmol) was heated at 80–90 °C for 3 h. After it cooled to room temperature, the components of the mixture were separated by flash chromatography (hexane).

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Compound **22** was obtained as a colorless oil (0.23 g, 33%): IR (neat) ν 3034, 2910, 1595, 1480, 1455, 1420, 1380, 1270, 1155, 1100, 900, 842, 725 cm^{-1}; ^{1}H NMR (60 MHz) δ 1.56 (d, J = 7 Hz, also contains a thiol proton, 4 H), 2.42–2.72 (m, 4 H), 3.98 (q, J = 7 Hz, 1 H), 7.15–7.72 (m, 9 H); exact mass calcd for $C_{16}H_{18}S_2$ 274.0844, found 274.0846.

Reaction of 22 with MeMgI Catalyzed by $NiCl_2(PPh_3)_2$. To a mixture of **22** (50.0 mg, 0.18 mmol), $NiCl_2(PPh_3)_2$ (8.0 mg, 0.012 mmol), and benzene (5 mL) under N_2 was added MeMgI (0.8 mL of a 1 M solution in Et_2O, 0.8 mmol). The mixture was stirred at room temperature for 24 h and then was quenched with saturated aqueous NH_4Cl. The two liquid layers were separated. The aqueous layer was extracted with Et_2O. The combined organic layers were washed with 10% aqueous NaOH and water and were dried (Na_2SO_4). After evaporation of the solvent in vacuo, the residue was purified by column chromatography on silica gel (hexane) to give **7g** (20 mg, 61%): mp 122–123 °C (lit.[41] mp 119–119.5 °C). The spectra of **7g** and those of an authentic sample were identical.

Reaction of 1 with *i*-PrMgBr. In a manner similar to that described in the general procedure, a mixture of **1** (262 mg, 1.01 mmol), $NiCl_2(PPh_3)_2$ (36 mg, 0.05 mmol), *i*-PrMgBr (1 M solution in Et_2O, 3 mL, 3 mmol), and benzene (5 mL) was stirred for 16 h at room temperature to afford a 6.7:1 mixture of 1,1-diphenyl-2-methylpropane (**25**) and 1,1-diphenyl-2-methylpropene (**26**) (158 mg, 76%). The two compounds were separated by preparative TLC (hexane). **25**:[41] IR (neat) ν 3025, 2950, 1595, 1445, 1382, 1165, 755, 740, 700 cm^{-1}; ^{1}H NMR (60 MHz) δ 0.85 (d, J = 6 Hz, 6 H), 2.45 (m, 1 H), 3.37 (d, J = 11 Hz, 1 H), 7.16 (s, 10 H); MS m/z (relative intensity) 211 (M^+ + 1, 1.9), 210 (M^+, 10.0), 167 (100.0), 152 (16.6), 115 (8.7), 91 (9.38). **26**:[43] IR (neat) ν 3050, 3010, 2900, 1650, 1595, 1485, 1435, 754, 685 cm^{-1}; ^{1}H NMR (60 MHz) δ 2.21 (s, 6 H), 7.16 (s, 10 H); MS m/z (relative intensity) 209 (M^+ + 1, 2.4), 208 (M^+, 9.8), 193 (100).

Reaction of 30 with Ethylmagnesium Bromide. The reaction of **30** (78.3 mg, 0.25 mmol) with EtMgBr (2 mL of a 1 M solution in Et_2O, 2 mmol) in toluene (3 mL) in the presence of $NiCl_2(PPh_3)_2$ (20 mg, 0.03 mmol), performed in a manner similar to that described in the general procedure, gave the reduction product **31**[44] (31 mg, 56%): bp 120 °C (1 mmHg Kugelrohr distillation); IR (neat) ν 3064, 2960, 1599, 1522, 1400, 1250, 1156, 1011, 845, 777, 692 cm^{-1}; ^{1}H NMR (60 MHz) δ 0.08 (s, 9 H), 2.67 (s, 2 H), 7.13–8.23 (m, 7 H); MS m/z (relative intensity) 214 (M^+, 0.84), 73 (base peak).

Isolation of the Dibenzyl Bisthioether (31) of 1,2-Ethanedithiol from the Reaction of 1 with MeMgI. A mixture of **1** (285 mg, 1.10 mmol), MeMgI (4 mL of a 1 M solution in Et_2O, 4 mmol), benzene (5 mL), and $NiCl_2(PPh_3)_2$ (60 mg, 0.09 mmol) was refluxed for 10 h. The mixture was quenched with 10% aqueous NaOH (5 mL) and benzyl bromide (400 mg, 2.3 mmol). The mixture was then refluxed for 4 h. After it cooled, it was poured into water (10 mL). The two liquid layers were separated. The aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with 10% aqueous NaOH (10 mL) and water (2 × 20 mL) and were dried (Na_2SO_4). After evaporation of the solvent in vacuo, the residue was purified by column chromatography on silica gel (hexane/EtOAc, 9:1) to give **31**[45] (129 mg, 47%): IR (neat) ν 3031, 1600, 1494, 1452, 1241, 1196, 1070, 1028, 768, 697 cm^{-1}; ^{1}H NMR (60 MHz) δ 2.53 (s, 4 H), 3.63 (s, 4 H), 7.20 (s, 10 H); MS m/z (relative intensity) 276 (M^+ + 2, 0.5), 274 (M^+, 4.4), 91 (base peak).

Detection of the Ethane Produced during the Reaction of MeMgI with $NiCl_2(PPh_3)_2$. To $NiCl_2(PPh_3)_2$ (0.5 g, 0.76 mmol) under N_2 were added, by syringe, benzene (5 mL) and MeMgI (1 mL of a 2.0 M solution in ether, 2 mmol). A reaction took place immediately. Heat was liberated, and the mixture turned dark brown. A sample of the vapor above the liquid phase was removed with a gas-tight syringe and was subjected to GC–MS analysis (GC temperature, 31 °C; MS electron beam energy, 11 eV). A peak in the spectrum at m/z 30 was attributed to ethane.

Detection of the $Me_3SiCH_2CH_2SiMe_3$ Produced during the Reaction of Me_3SiCH_2MgCl with $NiCl_2(PPh_3)_2$. In a manner similar to that described above, $NiCl_2(PPh_3)_2$ (0.5 g, 0.76 mmol) in benzene (10 mL) was allowed to react with Me_3SiCH_2MgCl (3.0 mL of a 2.0 M solution in Et_2O, 6.0 mmol). After the exothermic reaction subsided, the mixture was poured into saturated aqueous NH_4Cl and was extracted with Et_2O (3 × 10 mL). The combined extracts were washed with 10% aqueous NaOH (10 mL), water (10 mL), and brine (10 mL) and were dried ($MgSO_4$). The dried extract was analyzed by GC–MS (GC temperature, 57 °C; MS electron beam energy, 11 eV). A peak in the spectrum at m/z 174 was attributed to $Me_3SiCH_2CH_2SiMe_3$.

Detection of the Me_4Si Produced during the Reaction of Me_3SiCH_2MgCl with 1 in the Presence of $NiCl_2(PPh_3)_2$. Under N_2, to a mixture of **1** (523.7 mg, 2.0 mmol), $NiCl_2(PPh_3)_2$ (71.3 mg, 0.11 mmol), and benzene (15 mL) was added, by syringe, Me_3SiCH_2MgCl (4.0 mL of a 2 M solution in Et_2O, 8 mmol). The mixture was refluxed for 16 h. The solvent was then removed by distillation. The distillate was analyzed by GC–MS analysis (GC temperature, 45 °C; MS electron beam energy, 11 eV). A peak in the spectrum at m/z 88 was attributed to tetramethylsilane.

In a control experiment the reaction was performed under identical conditions, but in the absence of $NiCl_2(PPh_3)_2$. The solvent was removed by distillation. The distillate was analyzed by GC–MS (GC temperature, 45 °C; MS electron beam energy, 11 eV). The intensity of the peak at m/z 88 was less than one-tenth of that observed in the previous experiment.

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Supplementary Material Available: Physical properties of, and spectroscopic data on, **7a–g** and ^{1}H NMR spectra of **9**, **23**, and **32a–j** (13 pages). Ordering information is given on any current masthead page.

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