and Henry Dreyfus Teacher-Scholar Grant.

Registry No. 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$, 75059-90-4; 1,2-$Mo_2Me_2(CH_2SiMe_3)_4$, 75059-91-5; 1,1-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$, 75059-94-8; 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$, 76599-13-8; 1,1′-$Mo_2(NMe_2)(O_2CNMe_2)(CH_2SiMe_3)_4$, 76716-47-7; 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$, 75059-93-7; 1,2-$Mo_2(O\text{-}i\text{-}Pr)_2(CH_2SiMe_3)_4$, 75059-92-6; $Mo_2Br(CH_2SiMe_3)_5$, 79172-46-6; 1,1-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$, 75059-95-9; 1,2-$Mo_2Br(O\text{-}t\text{-}Bu)(CH_2SiMe_3)_4$, 79172-47-7; 1,2-$Mo_2MeBr(CH_2SiMe_3)_4$, 79172-75-1; $Mo_2(CH_2SiMe_3)_6$, 34439-17-3.

Supplementary Material Available: A listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page. The complete structural report, MSC Report 8024, is available in microfiche form only, from the Indiana University Library.

Unsaturated (π-Allyl)nickel Halide Complexes. Reactions To Produce Dienes

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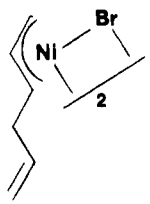
The (π-allyl)nickel halide complexes of 1-bromohexa-2,5-diene (1), 1-bromopenta-2,4-diene (2), 1-bromohexa-2,4-diene (3), and 2-(bromomethyl)-1,3-butadiene (4) were prepared from either nickel carbonyl or bis(cyclooctadiene)nickel and were characterized. The nonconjugated (π-1-(2-propenyl)allyl)nickel halide complex 1 reacted cleanly with iodobenzene, β-bromostyrene, cinnamyl bromide, iodocyclohexane, iodohexane, o-bromobenzamide, and o-bromoaniline to replace the halogen with the 1,4-hexadienyl group. The complexes from 1-bromopenta-2,4-diene (2) and 1-bromohexa-2,4-diene (3) were considerably less useful, reacting only with the very reactive substrates iodobenzene, cinnamyl bromide, and β-bromostyrene. The complex from 2-(bromomethyl)-1,3-butadiene (4) was used to synthesize myrcene, β-farnesene, and tagetol.

(π-Allyl)nickel halide complexes are easily prepared from the reaction of allylic halides with either nickel carbonyl or bis(cyclooctadiene)nickel in a nonpolar solvent such as benzene. The complexes are usually deep red crystalline, air-sensitive solids that can be stored in the absence of air for at least several years. In polar solvents such as DMF, they are generally reactive toward a wide range of organic halides, reacting to replace the halide in the substrate with the allyl group originally on nickel.[1] Under more severe conditions, some (π-allyl)nickel halide complexes react with ketones or aldehydes to produce homoallylic alcohols.[2] In relation to ongoing studies directed toward the synthesis of heterocycles by palladium-catalyzed cyclizations of amino olefins,[3-6] a number of diene-containing substrates were required. Although a number of new methods for the introduction of pentadienyl and hexadienyl groups into organic substrates have been recently reported,[7-9] none offered viable approaches to the desired substrates. Thus, we synthesized four new (π-allyl)nickel halide complexes containing an additional double bond and studied their reactions with organic halides and carbonyl compounds.

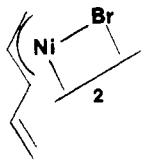
Results and Discussion

Preparation of (π-Allyl)nickel Halide Complexes

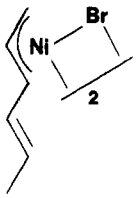
Complex 1 was prepared in 76% isolated yield on a 10-g



1



2



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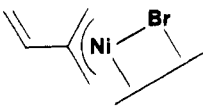

4

scale by the reaction of a mixture of 1-bromo-2,5-hexadiene and 3-bromo-1,5-hexadiene with nickel carbonyl in benzene at 70 °C. This stable red crystalline solid was a typical (π-allyl)nickel halide complex in both its physical and chemical characteristics. In that regard, complex 1 is similar to other nonconjugated, unsaturated (π-allyl)nickel halide complexes such as those containing π-geranyl ligands.[10]

(1) For reviews concerning the preparation and reactions of (π-allyl)nickel halides see: (a) M. F. Semmelhack and P. Helquist, *Org. Synth.* **52**, 115 (1972); (b) M. F. Semmelhack, *Org. React.*, **19**, 115 (1972); (c) R. Baker, *Chem. Rev.*, **73**, 787 (1973); (d) L. S. Hegedus, *J. Organomet. Chem. Libr.*, 1, 329 (1976).

(2) (a) E. J. Corey and M. F. Semmelhack, *J. Am. Chem. Soc.*, **89**, 2755 (1967); (b) L. S. Hegedus, S. D. Wagner, E. L. Waterman, and K. Siirala-Hansen, *J. Org. Chem.*, **40**, 593 (1975).

(3) D. E. Korte, L. S. Hegedus, and R. K. Wirth, *J. Org. Chem.*, **42**, 1329 (1977).

(4) L. S. Hegedus, G. F. Allen, J. J. Bozell, and E. L. Waterman, *J. Am. Chem. Soc.*, **100**, 5800 (1978).

(5) L. S. Hegedus, G. F. Allen, and D. J. Olsen, *J. Am. Chem. Soc.*, **102**, 3583 (1980).

(6) L. S. Hegedus, P. M. Winton, and S. Varaprath, *J. Org. Chem.*, **46**, 2215 (1981).

(7) For the Lewis acid catalyzed reactions of dienylsilanes with electrophiles see: A. Hosomi, M. Saito, and H. Sakurai, *Tetrahedron Lett.*, **21**, 3783 (1980).

(8) For an approach to the isoprene synthon see: S. R. Wilson, L. R. Phillips, and K. J. Natalie, Jr., *J. Am. Chem. Soc.*, **101**, 3340 (1979).

(9) C. A. Henrick, *Tetrahedron*, **33**, 1845 (1977).

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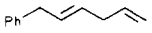
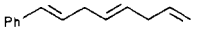
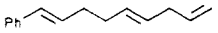
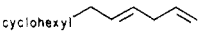
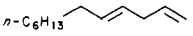
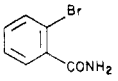
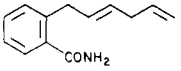
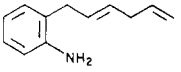
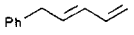
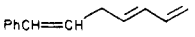
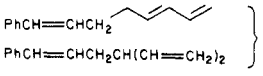
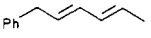
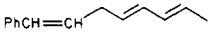
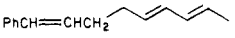
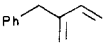
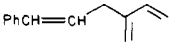
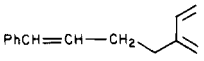
Table I. Reactions of (π-Allyl)nickel Halide Complexes 1-4 With Organic Halides

complex	halide	product	yield,[a] %
1	PhI		91
	PhCH=CHBr		96
	PhCH=CHCH$_2$Br		52
	cyclohexyl I		63
	n-C$_6$H$_{13}$I		51
			60
			51
2	PhI		45[b]
	PhCH=CHBr		69[b]
	PhCH=CHCH$_2$Br		28[b]
3	PhI		46
	PhCH=CHBr		60[b]
	PhCH=CHCH$_2$Br		23
4	PhI		46
	PhCH=CHBr		50
	PhCH=CHCH$_2$Br		52

[a] Reported yields are for isolated, purified products, based on the substrate halide as a limiting reagent. [b] Based on NMR integration and VPC analysis; crude product contaminated with tetraenes from self-coupling of allyl groups.

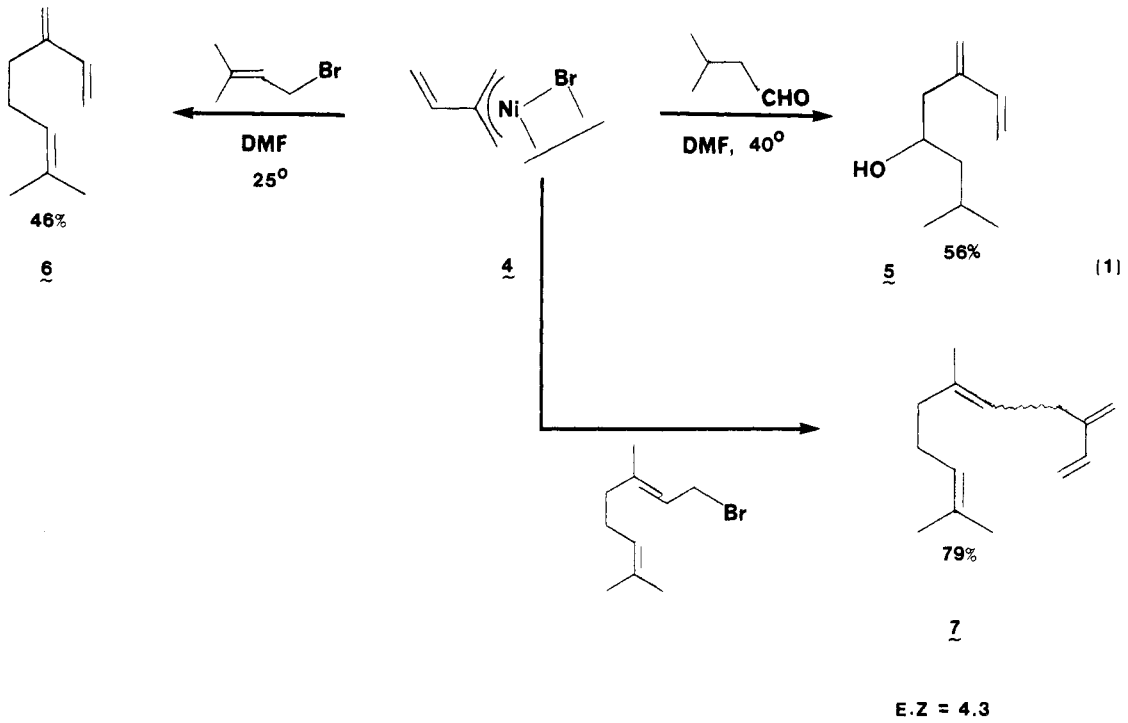
Complex 4 was best prepared by the reaction of 2-(bromomethyl)-1,3-butadiene with bis(cyclooctadiene)-nickel in benzene at 0 °C. Under these conditions a 74% isolated yield of this stable, red crystalline material was obtained. Attempts to prepare this complex from nickel carbonyl always resulted in lower yields of impure materials. The starting bromide was available in overall 53% yield from isoprene, by using a modification of a published procedure reported to proceed in only 11% yield.[11] Complex 4 was also a typical (π-allyl)nickel complex, and its NMR spectrum indicated no interaction of the cross-conjugated double bond with the metal.

In contrast, complexes 2 and 3 were much less tractable and have not been isolated and purified. Reaction of the requisite dienic bromides either with nickel carbonyl at 40 °C or with bis(cyclooctadiene)nickel at 0 °C led to initial formation of the deep red color indicative of formation of a (π-allyl)nickel halide complex followed by a fading of this color with concommitant deposition of nickel bromide. From these reactions, only self-coupling products (dimers) were obtained. The reaction of these allylic halides with nickel carbonyl in the absence of the solvent produced a deed red sticky solid, insoluble in organic solvents ranging from benzene to DMF. Thus, these complexes could not be isolated and purified. However, it was clear that they were being formed, and a procedure for their generation and subsequent reaction in situ was developed.

Reactions of Complexes 1-4 with Organic Substrates. The results of the reactions of complexes 1-4 with a variety of organic halides are summarized in Table I. Complex 1 was the most generally useful, reacting with aryl, vinyl, allyl, and saturated alkyl halides to introduce the nonconjugated 1,4-hexadienyl side chain in fair to excellent yield. Complexes 2-4 were considerably less general in their reactions.

Because of their instability complexes 2 and 3 were generated in situ by reaction of the allylic halide with bis(cyclooctadiene)nickel in THF at -30 °C followed by addition of the substrate. The reaction was stirred at 0 °C until the red color of the (π-allyl)nickel halide complexes had disappeared. Reactions run at temperatures in excess of 0 °C resulted in preferential decomposition of the nickel complex. Because of this instability only the most reactive of substrates (aryl iodides, vinyl, and allyl

(10) E. J. Corey, M. F. Semmelhack, and L. S. Hegedus, *J. Am. Chem. Soc.*, **90**, 2416 (1968).
(11) R. C. Krug and T. F. Yen, *J. Org. Chem.*, **21**, 1082 (1956).



bromides) were successfully allylated. The reaction with cinnamyl bromide suffered from the usual allyl–allyl interchange resulting in the formation of all possible coupling products, hence lowering the yield of the desired cross-coupled product.[10] Other substrates, including ketones and aldehydes, lacked sufficient reactivity to undergo allylation at temperatures below which complex decomposition occurred.

Complex 4 reacted with aryl, vinyl, and allyl halides to introduce the isoprenyl group into these substrates. This complex was used to synthesize three terpenoid compounds, myrcene, β-farnesene, and tagetol (eq 1). These results demonstrate three interesting features of complex 4. The formation of tagetol (5) indicates that 4 is sufficiently stable to survive the gentle heating necessary to effect reactions with aldehydes. This stands in direct contrast to the behavior of complexes 2 and 3. The reaction with isoprenyl bromide to form myrcene in 63% yield indicates that allyl–allyl exchange does not occur to a significant extent and that cross coupling to allylic halides with this complex is an efficient process. This is confirmed in the cross coupling with geranyl bromide to form β-farnesene in high yield. This reaction is particularly interesting in light of the fact that the reaction of (π-geranyl)nickel bromide with isoprenyl bromide gave β-farnesene in only 20% yield, with an *E*:*Z* ratio of 0.8.[12] Clearly the reaction depends on the exact nature of the (π-allyl)nickel halide complex involved, and complex 4 appears to be an attractive reagent for the introduction of the isoprenyl group in the synthesis of terpenes.

In summary, complexes 1–4 offer a method to introduce diene-containing units into a variety of substrates, particularly organic halides. Although in some instances, the yields are rather low, the procedure only involves one step and may prove to be more efficient than multistep approaches.

Experimental Section

General Data. Infrared (IR) spectra were recorded on a Beckman Model 4200 spectrophotometer. Proton NMR spectra were determined on a Varian T-60 or EM-360A spectrometer. All the chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Liquid chromatography was carried out at moderate pressures (40–80 psi) with either 15 × 250 mm or 15 × 1000 mm columns using Woelm type 206 silica gel. Preparative layer chromatography was carried out by using 20 × 20 cm plates coated with EM laboratories 60 PF-254 silica gel. Gas chromatography was done by using Bendix gas chromatograph 2300. Dry tetrahydrofuran (THF) and benzene were obtained by distillation from sodium. Dimethylformamide (DMF) was distilled over calcium hydride and under reduced pressure. Hexane was distilled over lithium aluminum hydride (LAH).

Preparation of π-Allylnickel Halide Complexes. (π-1-(2-Propenyl)allyl)nickel Bromide (1). This complex was prepared by the procedure of Semmelhack[1a] from *nickel carbonyl* (*Toxic! EXTREME Caution!*) (20 mL) and a mixture of 1-bromo-2,5-hexadiene and 3-bromo-1,5-hexadiene[13] (8 g) in benzene (200 mL) at 65–70 °C for 1 h. The product was recrystallized from hexane at −78 °C to give 8.3 g (77%) of the desired complex as a red, crystalline air-sensitive solid. Anal. Calcd for $C_{12}H_{18}Br_2Ni_2$: Ni, 26.70. Found: Ni, 26.30. In spite of repeated purification and careful sample preparations, the NMR spectrum of this complex was always very broad and ill-defined.

(π-2-Vinylallyl)nickel Bromide (4). This complex was obtained as a red, crystalline air-sensitive solid in 74% yield by allowing bis(1,5-cyclooctadiene)nickel(0) (1.42 g, 5.16 mmol) to react with 2-(bromomethyl)-1,3-butadiene[11] (0.75 g, 5.16 mmol) in benzene (75 mL) at 0 °C for 1 h and purifying the product by recrystallization from hexane following the general procedure.[1b] NMR (C_6D_6): δ 1.40 (s, 2, anti, CH), 2.80 (s, 2, syn, CH), 4.90 (d, J = 12 Hz, 1, cis, CH=CH_2), 5.18 (d, J = 20 Hz, 1, trans, CH=CH_2), 6.16 (d of d, J's = 12, 20 Hz, 1, CH=CH_2). Anal. Calcd for $C_{10}H_{14}Br_2Ni_2$: Ni, 28.52; Br, 38.87. Found: Ni, 28.39; Br, 38.47.

Reaction of Complex 1 with (a) Iodobenzene. Iodobenzene (0.33 g, 0.64 mmol) in 3 mL of DMF was added to the solution of the nickel complex (0.36 g, 0.82 mmol) in 10 mL of DMF and the mixture stirred at room temperature for 24 h. After the usual isolation (partitioning between dilute HCl and ether)[1b] the product was purified by preparative layer chromatography on silica gel developing with petroleum ether (R_f 0.6) to yield 0.24 g (91%) of 6-phenyl-1,4-hexadiene. NMR (CCl_4): δ 2.8 (t, J = 5 Hz, 2, =CCH_2C=), 3.3 (d, J = 5 Hz, 2, ArCH_2), 4.8–5.1 (m, 2, =CH_2), 5.5 (m, 3, CH=), 7.1 (m, 5, ArH). Mass spectrum: m/e 158 (M^+, parent ion). Anal. ($C_{12}H_{14}$): C, H.

(12) M. F. Semmelhack, Ph.D. Thesis, Harvard University, 1967. See also ref 1b, p 191.

(13) J. C. H. Hwa and H. Sims, "Organic Syntheses"; Coll. Vol. V, Wiley, New York, 1973, p 608.

(b) Cyclohexyl Iodide. The reaction was carried out in the usual manner using 0.47 g (1.10 mmol) of the nickel complex and 0.46 g (2.14 mmol) of cyclohexyl iodide in 10 mL of DMF. After the reaction was stirred at room temperature for 4 days, isolation in the usual manner, followed by evaporative distillation at 70 °C (4mmHg), yielded 0.22 g (62.6%) of a colorless oil. NMR ($CDCl_3$): δ 0.6–1.8 (m, 11, cyclohexyl-H), 1.8–2.0 (m, 2, $CH_2C{=}$), 2.8 (m, 2, $={}CCH_2C{=}$), 4.8–5.3 (m, 2, $C{=}CH_2$), 5.4–6.2 (m, 2, CH=). Anal. ($C_{12}H_{20}$): C, H.

(c) 2-Bromobenzamide. 2-Bromobenzamide (3.25 g, 16.2 mmol) dissolved in 10 mL of DMF was treated with 4.2 g (9.5 mmol) of the nickel complex in 60 mL of DMF and stirred at room temperature for 7 days. The crude product was isolated following the usual procedure and purified by medium-pressure liquid chromatography (4:1 ether/hexane) to obtain the pure product (1.95 g, 60%) as a white crystalline solid: mp 98–100 °C. NMR ($CDCl_3$): δ 2.8 (t, J = 5 Hz, 2, $={}CCH_2C{=}$), 3.6 (d, J = 5 Hz, 2, $ArCH_2$), 4.8–5.2 (m, 2, $={}CH_2$), 5.4–6.2 (m, 3, CH=), 6.5 (br, 2, NH), 7.1–7.7 (m, 4, ArH). IR (KBr): 3375 (NH), 1650 (C=O), 1620 (C=O), 1595, 1575 cm^{-1}. Anal. ($C_{13}H_{15}NO$): C, H, N.

(d) 2-Bromoaniline. The nickel complex (0.43 g, 1.0 mmol) in 15 mL of DMF was treated with 0.25 g (1.50 mmol) of 2-bromoaniline dissolved in 2 mL of DMF. The reaction mixture was stirred at room temperature for 5 days. After standard isolation, the crude brown oil, purified by preparative layer chromatography on silica gel developing with chloroform (R_f 0.54), gave the product as a pale yellow liquid (0.13 g, 51%). NMR ($CDCl_3$): δ 2.75 (m, 2, $={}CCH_2C{=}$), 3.15 (m, 2, $ArCH_2$), 3.45 (s, 2, NH_2), 4.75–5.2 (m, 2, $={}CH_2$), 5.35–6.2 (m, 3, CH=), 6.3–7.1 (m, 4, ArH). IR (neat): 3470 (NH), 3390 (NH) cm^{-1}. Anal. ($C_{12}H_{15}N$): C, H, N. Mass spectrum: m/e 173 (M^+, parent ion).

(e) β-Bromostyrene. To 0.87 g (1.97 mmol) of the complex dissolved in 10 mL of DMF was added *trans*-β-bromostyrene (0.36 g, 1.97 mmol), and the mixture was stirred for 3 days at room temperature. The usual isolation followed by medium-pressure liquid chromatography (MPLC) on silica gel eluting with hexane gave 0.350 g (96%) of the product as a colorless oil. NMR (CCl_4): 2.8 (br m, 4, CH_2), 4.8–5.2 (m, 2, $={}CH_2$), 5.35–5.9 (m, 3, $={}C_{4,5,7}H$), 6.2 (t, J = 5 Hz, 1, $={}C_2H$), 6.35 (d, J = 16 Hz, 1, C_1H), 7.26 (s, 5, ArH). Anal. ($C_{14}H_{16}$): C, H.

(f) 1-Iodohexane. Reaction of the complex (1.10 g, 2.5 mmol) with 1-iodohexane (0.53 g, 2.5 mmol) for 3 days at room temperature followed by the usual isolation and evaporative distillation gave the pure product (0.21 g, 50.6%) whose NMR spectrum was identical with that previously reported.[14]

(g) Cinnamyl Bromide. The complex (0.68 g, 1.53 mmol) was treated with *trans*-cinnamyl bromide (0.30 g, 1.53 mmol) in THF (10 mL) and stirred at room temperature for 3 days. After the usual isolation procedure, purification by medium-pressure liquid chromatography on silica gel eluted with hexane gave a colorless oil in 52% yield (0.16 g). NMR (CCl_4): δ 2.1–2.43 (m, 4, CH_2CH_2), 2.7 (m, 2, $CCH_2C{=}$), 4.71–5.2 (m, 2, $={}CH_2$), 5.2–5.9 (m, 3, =CH), 6.1 (t, 1, J = 4 Hz, PhCHC*H*), 6.16 (d, J = 16 Hz, 1, PhC*H*=CH), 7.14 (s, 5, ArH). Anal. ($C_{15}H_{18}$): C, H.

General Procedure for the Reaction of Complex 2 with Halides. Bis(1,5-cyclooctadiene)nickel was dissolved in THF (20 mL/mmol) under an argon atmosphere. It was cooled to −30 °C, and 1-bromo-2,4-pentadiene was added while stirring the mixture rapidly. This was immediately followed by the rapid addition of the substrate, either as a neat liquid or as a solution in THF. The reaction mixture was kept initially at this temperature for 4 h and then at −20 °C for 1 h. It was then warmed to 0 °C and kept at this temperature until the red color disappeared. After the mixture was warmed to room temperature, water (5 mL) was added to dissolve the nickel salts, and THF was removed under vacuum. The product was extracted with ether, washed with water, followed by brine, dried ($MgSO_4$), and concentrated. The same general procedure was used in the reactions of complex 3 with halides.

Reaction of Complex 2 with (a) Iodobenzene. Reaction of the complex formed from 1.21 g (4.4 mmol) of bis(1,5-cyclooctadiene)nickel and 1-bromo-2,4-pentadiene (0.65 g, 4.4 mmol) with iodobenzene (0.45 g, 2.2 mmol) in THF in the manner described above gave, after purification by MPLC on silica gel eluted with hexane, 0.23 g of a colorless oil containing 45% (based on NMR) of 1-phenyl-2,4-pentadiene.[15] A sample of pure material was collected by preparative GLC (10 ft 10% Carbowax, 20M 110 °C, 3.8 min). NMR (CCl_4): δ 3.4 (d, J = 6 Hz, 2, $ArCH_2$), 4.8–6.6 (m, 5, =CH, $={}CH_2$), 7.16 (s, 5, ArH). Anal. ($C_{11}H_{12}$): C, H.

(b) β-Bromostyrene. Reaction of $Ni(COD)_2$ (1.88 g, 6.82 mmol), 1-bromo-2,4-pentadiene (1.0 g, 6.82 mmol), and *trans*-β-bromostyrene (0.624 g, 3.41 mmol) in THF gave after the usual isolation and MPLC separation (silica gel, hexane) 0.70 g of an oil containing 69% of the product (based on NMR). Pure product was obtained by preparative GLC (10 ft 10% Carbowax, 20M 180 °C, 8 min). NMR (CCl_4): δ 2.96 (t, J = 5 Hz, 2, CH_2), 4.8–5.3 (m, 2, $={}CH_2$), 5.53–6.4 (m, 3, =CH), 6.2 (t, J = 5 Hz, 1, PhCH=C*H*), 6.3 (d, J = 16 Hz, 1, PhC*H*=CH), 7.26 (s, 5, ArH). Mass spectrum: m/e 170 (M^+, parent ion). Anal. ($C_{13}H_{14}$): C, H.

(c) Cinnamyl Bromide. The procedure was slightly modified. To $Ni(COD)_2$ (1.68 g, 6.1 mmol) dissolved in THF (10 mL) was added triphenylphosphine dissolved in THF (1.50 g, 5.7 mmol). After 0.25 h, 1-bromo-2,4-pentadiene (0.90 g, 6.12 mmol) was added. The mixture was warmed to 25 °C and cinnamyl bromide (0.60 g, 3.06 mmol) was added. The isolation, after 3 days, following a partial separation (MPLC, silica gel, hexane) gave 410 mg of an oil containing 28% (by NMR) of the product as a 1:1 mixture of trienes. The mixture was separated by preparative GLC (10 ft 10% Carbowax, 150 °C; retention time, 12 min) to afford the pure compounds. NMR (CCl_4) (1-phenyl-1,5,7-octatriene): 2.2 (m, 4, CH_2CH_2), 4.8–5.36 (m, 2, $={}CH_2$), 5.66–6.56 (m, 4, =CH), 6.3 (d, J = 16 Hz, 1, PhC*H*=CH), 7.23 (s, 5, ArH). Anal. ($C_{14}H_{16}$): C, H. NMR (CCl_4) (1-phenyl-4-vinyl-1,5-hexadiene): 2.5 (t, J = 6 Hz, 2, CH_2), 3.06–3.53 (m, 1, CH), 4.8–6.5 (m, 8, $={}CH_2$, =CH), 7.23 (s, 5, ArH). Anal. ($C_{14}H_{16}$): C, H.

Reaction of Complex 3 with (a) Iodobenzene. Reaction of $Ni(COD)_2$ (1.16 g, 4.21 mmol), 1-bromo-2,4-hexadiene (0.68 g, 4.21 mmol), and iodobenzene (0.43 g, 2.1 mmol) gave, as described for complex 2 above after routine isolation procedures and purification (MPLC, silica gel, hexane) 0.15 g (46%) of pure product[16] as a colorless oil. NMR (CCl_4): δ 1.75 (d, J = 6 Hz, 3, CH_3), 3.33 (d, J = 6 Hz, 2, CH_2), 5.0–6.33 (m, 4, =CH), 7.2 (s, 5, ArH).

(b) β-Bromostyrene. Treatment of $Ni(COD)_2$ (1.31 g, 4.76 mmol) with 1-bromo-2,4-hexadiene (0.77 g, 4.76 mmol) and *trans*-β-bromostyrene (0.44 g, 2.38 mmol) in THF followed by isolation in the usual manner and the purification on silica gel by MPLC eluting with hexane gave an oil (520 mg) containing the product (60% based on NMR). It was separated by preparative GLC (10 ft 10% Carbowax, 180 °C, retention time, 9 min). NMR (CCl_4): δ 1.7 (d, J = 6 Hz, 3, CH_3), 2.9 (t, J = 6 Hz, 2, CH_2), 5.2–6.6 (m, 5, $={}CH_2$), 6.3 (d, J = 16 Hz, 1, α-H, PhC*H*=CH), 7.15 (s, 5, ArH). Mass spectrum: m/e 184 (M^+, parent ion). Anal. ($C_{14}H_{16}$): C, H.

(c) Cinnamyl Bromide. The modified procedure involving the use of triphenylphosphine is analogous to that reported earlier for the synthesis of 1-phenyl-1,5,7-octatriene. Thus reaction of $Ni(COD)_2$ (1.30 g, 4.7 mmol), 1-bromo-2,4-hexadiene (0.764 g, 4.7 mmol), cinnamyl bromide (0.47 g, 2.37 mmol), and triphenylphosphine (1.24 g, 4.7 mmol) yielded the product (110 mg, 23%) as an oil after separation by MPLC (silica gel, hexane). NMR (CCl_4): δ 1.66 (d, J = 6 Hz, 3, CH_3), 2–2.5 (m, 4, CH_2), 4.7–6.4 (m, 6, =CH), 7.2 (s, 5, ArH). Mass spectrum: m/e 198 (M^+, parent ion). Anal. ($C_{15}H_{18}$): C, H.

Reactions of Complex 4 with (a) Iodobenzene. The nickel complex (0.40 g, 1.09 mmol) cooled to −30 °C was dissolved in 10 mL of DMF also cooled to the same temperature. To the resulting solution was added iodobenzene (0.22 g, 1.09 mmol), and the mixture was warmed to room temperature and stirred for 1 day. The usual isolation followed by purification by medium-pressure liquid chromatography (hexane) gave 72 mg (46%) of the pure product[17] as a colorless oil. NMR (CCl_4): δ 3.5 (s, 2, $ArCH_2$), 4.8–5.4 (m, 4, $={}CH_2$), 6.4 (dd, J = 10 and 16 Hz, 1, =CH),

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7.2 (s, 5, ArH). Anal. ($C_{11}H_{12}$): C, H.

(b) β-Bromostyrene. To the nickel complex (0.97 g, 2.63 mmol) cooled to −30 °C was added the solution of *trans*-β-bromostyrene (0.43 g, 2.36 mmol) in DMF (10 mL) also cooled to −30 °C. the mixture was warmed to room temperature and stirred for 2 days. The isolation in the usual manner followed by separation on silica gel by MPLC with hexane as eluant gave 0.20 g (49.8%) of the desired product as a colorless oil. NMR (CCl_4): δ 3.06 (dd, J = 4 Hz, 2, CH_2), 4.93–5.4 (m, 4, =CH_2), 6.2–6.6 (m, 2, =CH), 6.4 (dd, J = 10 and 16 Hz, 1, PhCHC*H*), 7.2 (s, 5, ArH). Anal. ($C_{13}H_{14}$): C, H. Mass spectrum: m/e 170 (M^+, parent ion).

(c) Cinnamyl Bromide. The reaction of the nickel complex (0.738 g, 1.78 mmol) with cinnamyl bromide (0.35 g, 1.78 mmol) in THF (20 mL) was carried out in a fashion similar to that described above. Purification by MPLC on silica gel using hexane for elution gave 52% (0.17 g) of the desired product. NMR (CCl_4): δ 2.4 (m, 4, CH_2), 4.8–5.35 (m, 4, =CH_2), 5.6–6.8 (m, 3, =CH), 7.25 (s, 5, ArH). Mass spectrum: m/e 184 (M^+, parent ion).

Synthesis of Myrcene (6). To the freshly prepared nickel complex (0.62 g, 1.5 mmol) dissolved in THF (15 mL) was added 1-bromo-3-methyl-2-butene (0.34 g, 2.26 mmol) rapidly via a syringe. After being stirred for 20 h at room temperature, the mixture was filtered to remove the brownish yellow solid which was repeatedly washed with pentane. The filtrate was washed with water to remove THF and dried over $MgSO_4$. Pentane was removed by distillation to obtain an oil (0.25 g) containing 63% of myrcene.[18] Preparative layer chromatography on silica gel developing with hexane (R_f 0.51) gave the pure product (0.13 g, 46%) in all respects identical with the authentic material.

β-Farnesene. With use of 0.26 g (0.62 mmol) of the nickel complex and 0.20 g (0.93 mmol) of *trans*-geranyl bromide, the reaction was carried out as in the case of myrcene. Isolation and purification by the procedure similar to that described for myrcene gave 0.15 g (78.5%) of the product mixture of (*E*)- and (*Z*)-β-farnesene in the ratios of 81.3 and 18.6, respectively (calculated based on GLC). NMR and IR spectra of the product were as reported for β-farnesene.[19]

Tagetol. The nickel complex (0.85 g, 2.0 mmol) and isovaleraldehyde (0.27 g, 3.1 mmol) were allowed to react in THF at room temperature for 20 h and at 40 °C for 6 h. The reaction mixture was treated with 1 mL of water and diluted with 20 mL of ether. The organic layer was separated, washed with brine, dried ($MgSO_4$), and concentrated under rotary evaporator to obtain a yellow oil which was purified by preparative layer chromatography (Si gel, 2:1 hexane:ether, R_f 0.58) (yield, 0.27 g (56%)). ^1H NMR and IR spectra were identical with that of tagetol.[20]

Preparation of Allylic Bromides. The allylic bromides for the synthesis of complexes 1–3, 1-bromo-2,5-hexadiene,[13] 1-bromo-2,4-pentadiene,[21] and 1-bromo-2,4-hexadiene,[21] were synthesized by published procedures. The 2-(bromomethyl)-1,3-butadiene required for complex 4 was synthesized from 3-methyl-2,5-dihydrothiophene 1,1-dioxide (from isoprene and SO_2)[22] by the following procedure.

3-(Bromomethyl)-2,5-dihydrothiophene 1-Oxide (13). Freshly distilled methylene chloride (400 mL) was added to a mixture containing 35 g (0.26 mol) of 3-methyl-2,5-dihydrothiophene 1,1-dioxide and 47.2 g (0.26 mol) of recrystallized *N*-bromosuccinimide and 3 g of benzoyl peroxide. The mixture was stirred and heated at gentle reflux in an oil bath kept at 50 °C. The reaction flask was simultaneously irradiated with light from 500-W tungsten bulb to hasten the reaction. The reaction was followed by TLC on silica gel developing with ethyl acetate. Once all the NBS had been consumed, the flask was cooled to 25 °C and the solution filtered to remove the succinimide (25.0 g, 86.2%). The solvent was removed under vacuum and the product recrystallized from 95% ethanol (41.0 g, 73.0%); mp 87–88 °C (lit.[22] 87–88 °C). ^1H NMR (CCl_4): δ 6.0 (m, 1, =CH), 4.03 (s, 2, CH_2Br), 3.83 (s, 4, CH_2SO_2).

The (14) 2-(bromomethyl)-2,5-dihydrothiophene 1,1-dioxide (3.1 g) was placed in a short-path distillation apparatus. At a reduced pressure of 1mmHg the flask was immersed rapidly in an oil bath at 180 °C. No radical scavanger was added to the distillation flask. The product (1.56 g, 72%) was collected in a flask and cooled in Dry Ice/2-propanol bath. ^1H NMR (CCl_4): δ 4.26 (s, 2, CH_2Br), 5.4 (m, 4, =CH), 6.5 (m, 1, =CH).

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Registry No. 1, 79483-21-9; 2, 79483-22-0; 3, 79483-23-1; 4, 79483-24-2; 5, 35628-05-8; 6, 123-35-3; 7-(*E*), 502-60-3; 7-(*Z*), 28973-97-9; 13, 79482-77-2; 14, 31554-48-0; iodobenzene, 591-50-4; cyclohexyl iodide, 626-62-0; 2-bromobenzamide, 4001-73-4; 2-bromoaniline, 615-36-1; *trans*-β-bromostyrene, 588-72-7; 1-iodohexane, 638-45-9; 1-bromo-3-methyl-2-butene, 870-63-3; *trans*-geranyl bromide, 6138-90-5; isovaleraldehyde, 590-86-3; *trans*-cinnamyl bromide, 26146-77-0; 6-phenyl-1,4-hexadiene, 79482-78-3; 6-cyclohexyl-1,4-hexadiene, 79482-79-4; 2-(2,5-hexadienyl)benzamide, 76916-63-7; 2-(2,5-hexadienyl)aniline, 76916-50-2; 1-phenyl-1,4,7-octatriene, 79482-80-7; 1,4-dodecadiene, 79482-81-8; 9-phenyl-1,4,8-nonatriene, 79482-82-9; 5-bromo-1,3-pentadiene, 1001-93-0; 5-phenyl-1,3-pentadiene, 1007-52-9; 7-phenyl-1,3,6-heptatriene, 79482-83-0; 1-phenyl-1,5,7-octatriene, 79482-84-1; 1-phenyl-4-vinyl-1,5-hexadiene, 79482-85-2; 6-phenyl-2,4-hexadiene, 79482-86-3; 8-phenyl-2,4,7-octatriene, 79482-87-4; 9-phenyl-2,4,8-nonatriene, 79482-88-5; 3-methylene-4-phenyl-1-butene, 16079-66-6; 3-methylene-6-phenyl-1,5-hexadiene, 79482-89-6; 3-methyl-7-phenyl-1,6-heptadiene, 79482-90-9; 3-methyl-2,5-dihydrothiophene 1,1-dioxide, 1193-10-8; nickel tetracarbonyl, 13463-39-3; bis(1,5-cyclooctadiene)nickel (0), 1295-35-8; 6-bromo-1,4-hexadiene, 5903-38-8; 3-bromo-1,5-hexadiene, 53737-88-5; 2-(bromomethyl)-1,3-butadiene, 23691-13-6; 1-bromo-2,4-hexadiene, 63072-78-6.

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