2-(Carboethoxy)-5,5-dimethyl-3-methyl-3,4,6-trihydro-2*H*-pentalen-1-one (21). From tin(IV) cyclization of **17**: ^{1}H NMR (CCl_4) δ 4.13 (q, 2 H, J = 7 Hz), 2.70–2.30 (m, 2 H), 2.03 (s, 2 H), 2.00–1.65 (m, 2 H), 1.27 (t, 3 H, J = 7 Hz), 1.20 (d, 3 H, J = 6 Hz), 1.15 (s, 3 H), 1.00 (s, 3 H); IR (CCl_4 soln) cm^{-1} $\nu_{C=O}$ 1730 (with shoulder at 1760), 1680, $\nu_{C=C}$ 1640, enol OH ν_{OH} 3200; ^{13}C NMR ($CDCl_3$) δ 171.42, 169.85, 121.64, 105.22, 60.48, 57.93, 53.22, 48.61, 40.54, 39.46, 28.79, 27.78, 20.71, 14.27; mass spectrum, m/e 236 (M^+), 57 (base), 180, 124, 71, 169, 83, 191, and 109 (30%).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.14; H, 8.55. Found: C, 71.02; H, 8.52.

2-(Carboethoxy)-3-methyl-3,4,5,6,7-pentahydro-2*H*-inden-1-one (22). From iodotrimethylsilane cyclization of **18**: ^{1}H NMR (CCl_4) δ 4.10 (q, 2 H, J = 7 Hz), 3.20–2.80 (m, 2 H), 2.40–1.50 (two br m, 8 H), 1.27 (t, 3 H, J = 7 Hz), 1.20 (d, 3 H, J = 6 Hz); IR ($CDCl_3$ soln) cm^{-1} $\nu_{C=O}$ 1735, 1710, $\nu_{C=C}$ 1645, enol OH (weak) ν_{OH} 3400; ^{13}C NMR ($CDCl_3$) δ 200.46, 176.73, 169.53, 136.48, 61.29, 60.15, 40.97, 25.86, 21.96, 21.42, 20.06, 17.68, 14.16; mass spectrum, m/e 222 (M^+), 148 (base), 133, 79, 91, 105, 177, 121, and 55 (48%).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.23; H, 8.18. Found: C, 70.20; H, 8.16.

2-(Carboethoxy)-3-methyl-3,4,5,6,7,8-hexahydro-2*H*-azulen-1-one (23). From iodotrimethylsilane cyclization of **19**: ^{1}H NMR (CCl_4) δ 4.12 (q, 2 H, J = 7 Hz), 3.10–2.70 (m, 2 H), 2.55–2.10 (m, 4 H), 1.80–1.30 (m, 6 H), 1.27 (t, 3 H, J = 7 Hz), 1.20 (d, 3 H, J = 6 Hz); IR (liquid film) cm^{-1} $\nu_{C=O}$ 1740, 1710, $\nu_{C=C}$ 1650; ^{13}C NMR ($CDCl_3$) δ 200.40, 180.36, 169.31, 140.32, 61.28, 59.93, 41.62, 31.17, 30.95, 26.34, 26.14, 23.31, 18.05, 14.16; mass spectrum, m/e 236 (M^+), 162 (base), 91, 79, 54, 133, 190, 68, and 147 (35%).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.14; H, 8.55. Found: C, 70.96; H, 8.49.

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Registry No. 5, 71068-74-1; **6**, 78064-71-8; **9**, 78064-72-9; **10**, 78090-04-7; **11a**, 78063-95-3; **11b**, 78063-96-4; **11c**, 78063-97-5; **13**, 78064-73-0; **14**, 13176-53-9; **15**, 78064-74-1; **16**, 78064-75-2; **17**, 78064-76-3; **18**, 78064-77-4; **19**, 78064-78-5; **20**, 78064-79-6; **21**, 78064-80-9; **22**, 78064-81-0; **23**, 78064-82-1; crotonoyl chloride, 10487-71-5; cinnamoyl chloride, 102-92-1; 1-cyclopentene-1-carboxylic acid chloride, 59253-90-6; 3,3-dimethyl-1-cyclopentene-1-carboxylic acid chloride, 78064-83-2; 1-cyclohexene-1-carboxylic acid chloride, 36278-22-5; 1-cycloheptene-1-carboxylic acid chloride, 72233-47-7; methyl 2-bromopropenoate, 4519-46-4; ethyl propiolate, 623-47-2; 2-(carbomethoxy)-3-(cyclohexen-1-yl)-1-buten-3-ol, 58371-16-7; 1-acetyl-1-cyclohexene, 932-66-1; ethyl 2-deuteriocrotonate, 78064-84-3; ethyl 2-ethylidene-3-(1-cyclohexen-1-yl)-3-hydroxybutanoate, 78064-85-4.

Terpene Amine Synthesis via Palladium-Catalyzed Isoprene Telomerization with Ammonia

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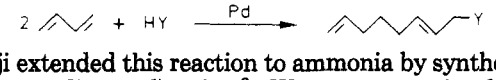
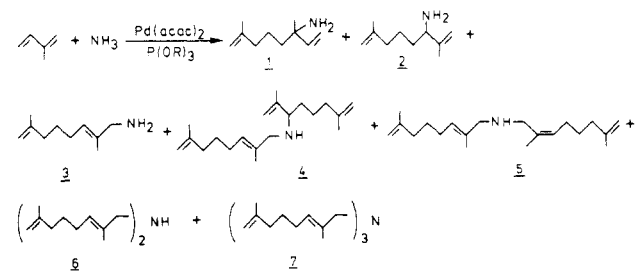
Isoprene and dry ammonia could be converted in a catalytic process in good yields into a mixture of primary, secondary, and tertiary terpene amines. Homogeneous catalysts formed from palladium acetylacetonate and tributyl phosphite showed the best activities and selectivities for the telomerization. Seven amines were isolated as the main products from the reaction mixture and were characterized by their spectral data. Tail-to-tail coupling of the isoprene units was predominant though under certain conditions α-linalylamine, which shows a head-to-tail structure, prevailed. The product distribution could be controlled by cocatalysts and reaction parameters. The formation of primary terpene amines was favored by short reaction times and high ammonia/isoprene ratios. The proper choice of solvents and especially ligands is shown to be essential, and a strong dependence on the catalyst concentration was observed. A mechanism involving bridged binuclear palladium complexes as the active species is discussed.

The telomerization of 1,3-dienes with nucleophiles catalyzed by homogeneous catalysts has been of considerable interest in the recent literature.[1,2] A variety of nucleophiles such as alcohols, amines, acids, and water undergo this reaction, affording predominantly 2,7-octadienyl derivatives.



Tsuji extended this reaction to ammonia by synthesizing tris(2,7-octadien-1-yl)amine.[3] We now report for the first time the telomerization of isoprene and ammonia to yield a spectrum of novel terpene amines. The dimerization of isoprene and the concomitant addition of ammonia represents a potential and facile route to aminated terpene products, useful as starting material for insecticides and fungicides. By considering tail-to-tail, tail-to-head, head-to-tail, and head-to-head dimerizations of the isoprene

Scheme I



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(2) J. Tsuji, *Acc. Chem. Res.*, **6**, 8 (1973).
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Table I. Palladium-Catalyzed Codimerization of Isoprene and Ammonia with Different Ligands

expt	ligand	$\Sigma\chi_i$,[c] cm^{-1}	cone angle,[c] deg	% yield	% selectivity: amines 1-7	1	2	3	4	5	6	7
1	$P(OCH_3)_3$	23.4	107 ± 2	7	48	6	15	14	4	3	6	0.4
2	$P(OC_2H_5)_3$	20.2	109 ± 2	44	62	6	9	4	13	5	10	15
3	$P(O\text{-}n\text{-}C_4H_9)_3$	19.5	110[a]	53	64	5	12	5	13	6	11	12
4	$P(O\text{-}i\text{-}C_3H_7)_3$	19.8	130 ± 2	68	40	2	20	3	11	2	2	0.3
5	$P(OCH_2CH{=}CH_2)_3$	22.6	110[a]	2								
6	$P(OC_6H_5)_3$	29.2	121 ± 10	<1								
7	$P(n\text{-}C_4H_9)_3$	4.2	130 ± 4	82	10	0.5	3	0.6	3	2	1	
8	$P(c\text{-}C_6H_{11})_3$	0.3	179 ± 10	3								
9	$P(C_6H_5)_3$	12.8	145 ± 10	28	44	5	16	4	7	4	6	2

[a] These cone angles are estimated; reactions were carried out in 75-mL stainless-steel autoclaves with 0.5 mmol of $Pd(acac)_2$, 1.5 mmol of ligand, 25 mL of CH_3CN as solvent, 0.2 mol of isoprene, 0.2 mol of dry ammonia, and 1.0 g of CO_2 under an argon atmosphere at 100 °C for 20 h. [b] Yields were calculated as the quotient of reaction products/isoprene (w/w). [c] $\Sigma\chi_i$ values and cone angles taken from literature.[4,5,8,9]

Table II. Preformed ML_4 Complexes as Catalyst[a]

expt	catalyst	% yield[b]	product composition by GC, %: amines 1-7	1	2	3	4	5	6	7
10	$Ni[P(OC_2H_5)_3]_4$	3								
11	$Pd[P(OC_2H_5)_3]_4$	33	46	6	13	9	5	3	6	4
12	$Pd[P(O\text{-}n\text{-}C_4H_9)_3]_4$	48	45	5	9	5	7	4	7	8
13	$Pd[Ph_3P]_4$	37	51	3	12	7	8	5	8	8
14	$Pt[P(OC_2H_5)_3]_4$	12								
15	$Pt[PPh_3]_4$	16	31	4	14	5	3	2	2	1

[a] Reaction conditions: 0.5 mmol of complex, 25 mL of CH_3CN, 0.2 mol of isoprene, 0.2 mol of NH_3, 120 °C temperature, 20-h reaction time, stainless-steel autoclave. [b] Quotient of reaction product/isoprene (w/w).

moiety, one can visualize a variety of terpene amines, and tailoring of the product distribution is a major challenge in this type of catalysis.

Results and Discussion

A catalyst consisting of palladium acetylacetonate and phosphites converts isoprene and dry ammonia to a mixture of terpene amines and isoprene dimers such as 2,7-dimethyl-1,3,7-octatriene, dipentene, and diprene. The amines 1–7 could be isolated by distillation and GC (see Scheme I). Definitive identification and structural assignment of these amines rests on IR, mass, and ^1H NMR spectra as well as on elemental analysis.

The formation of the primary (1–3) secondary (4–6), and tertiary amines shows that all three hydrogens of the NH_3 molecule can participate, opening the way to a spectrum of possible derivatives.

It is well established that in this type of homogeneous, transition-metal-catalyzed reaction the selectivity can be steered by selecting the right ligands. However, the understanding of the ligand properties needed is lacking, and often "trial and error" provides the only approach. In general terms, steric and electronic effects are discussed to account for the influence of ligands. For instance, Tolman introduced the concept of cone angles and $\Sigma\chi_i$ values.[4,5] The latter one describes the σ-donor and π-back-bonding ability. The cone angles give some measurement for the steric hindrance. It should be emphasized that this characterization is not generally accepted.[6,7]

In our efforts to develop highly active catalytic systems, numerous experiments were carried out with a variety of phosphorous ligands. Table I lists the results obtained with various phosphines and phosphites. Tri-*n*-alkyl phosphites having cone angles of 107–110° and $\Sigma\chi_i$ values between 19 and 23 proved to be the best ligands in the telomerization reaction of isoprene and ammonia. It is also evident from Table I that ligands with lower $\Sigma\chi_i$ values or higher cone angles yield poorer results.

These findings are in agreement with Tolman's approach. Isoprene, ammonia, and the ligands compete for coordination sites on the palladium metal. Phosphites form strong bonds to transition metals and thus stabilize the catalytic active species. In addition, they lower the electron density of the palladium metal by π back-bonding which facilitates the nucleophilic attack of ammonia. This is emphasized by the finding that the more basic trialkylphosphines yield mainly isoprene dimers instead of aminated products (exp 7). When phosphines with high steric hindrance are applied, the coordination of isoprene is blocked, and neither dimerization nor telomerization occurs.

Further studies focussed on $P(O\text{-}n\text{-}C_4H_9)_3/Pd(acac)_2$ as the catalyst system. A reaction temperature of 120 °C and a reaction time of 20 h turned out to be appropriate for best yields and selectivities.

The activation of the palladium-catalyzed telomerization reaction by the addition of CO_2 has been reported in the literature.[10,11] We observed at low reaction temperatures and with phosphines as ligands significant enhancement of conversion rates upon addition of carbon dioxide.

The competition for coordination sites must be affected by the ligand concentration applied. Indeed, as it is elucidated in Figure 1, the best ratio is obtained at Pd/ligand

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(10) K. E. Atkins, W. E. Walker, and R. M. Manyik, *Chem, Commun.*, 7, 330 (1971).
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Table III. Influence of the Ammonia/Isoprene Ratio[a]

expt	ammonia/ isoprene molar ratio	% yield	product composition by GC, %: amines 1-7	1	2	3	4	5	6	7
16	1/6	69	56	1	5	2	14	5	10	19
17	1/1	69	63	3	9	5	13	7	12	14
18	5/1	19	78	7	24	34	4	3	6	0.4

[a] Conditions: 0.5 mmol of $Pd(acac)_2$, 2.0 mmol of $P(OBu)_3$, 25 mL of CH_3CN, 0.2 mol of isoprene, 0.033–1.0 mol of NH_3; 120 °C temperature; 20-h reaction time, stainless-steel autoclave. [b] Quotient of reaction products/isoprene.

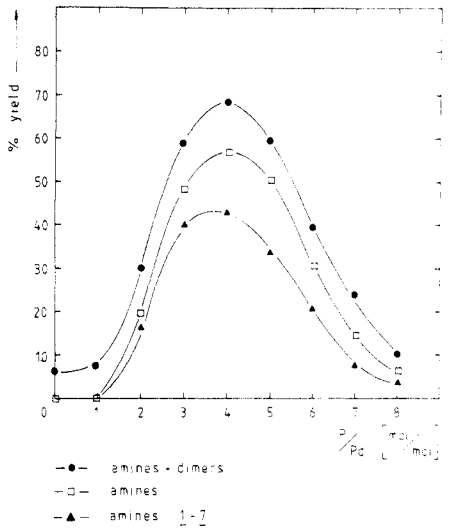


Figure 1. Influence of the molar ratio of $Pd(acac)_2/P(OBu)_3$ on the codimerization of isoprene and ammonia. Conditions: 0.5 mmol of $Pd(acac)_2$, 0–4.0 mmol of $P(OBu)_3$, 25 mL of CH_3CN, 0.2 mol of isoprene, 0.2 mol of NH_3, reaction time 20 h, temperature 120 °C, stainless-steel autoclave.

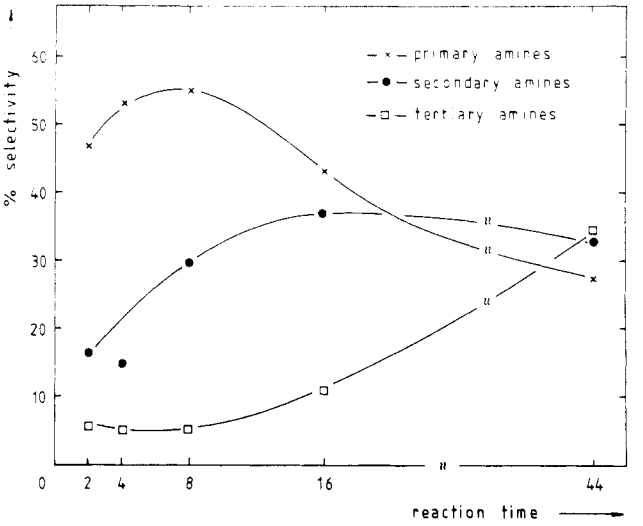


Figure 2. Influence of the reaction time on the product distribution of the terpene amine synthesis. Conditions: 0.5 mmol of $Pd(acac)_2$; 2.0 mmol of $P(OBu)_3$, 25 mL of CH_3CN, 0.2 mol of isoprene, 0.2 mol of NH_3, reaction temperature 100 °C, stainless-steel autoclave (see also expt 16–18, Table III).

ratios of 1:4. Under these conditions isoprene and ammonia could be converted in a 69% yield to 63% amines 1–7. Higher ligand to palladium ratios may block the coordination of isoprene and ammonia. Lower ligand to palladium ratios destabilize the catalyst as is evident from the formation of elemental palladium during the reaction.

The reduction of $Pd(acac)_2$ by phosphites in the presence of amines is known from the literature and can be utilized to synthesize $Pd[P(OR)_3]_4$ complexes.[12] Therefore, it was of interest to start directly from the corresponding $Pd[P(OR)_3]_4$ complexes (Table II). The results are in agreement with those of Table I, yet yields and selectivities are somewhat lower. This can be understood by the high stability of $Pd[P(OR)_3]_4$ complexes. Prior to the formation of active species, ligand dissociation must occur.

For the investigation of metals other than palladium for this telomerization, the complexes $Ni[P(OEt)_3]_4$, $Pt[P(OEt)_3]_4$ and $Pt(PPh_3)_4$ were also applied. The nickel complex was inactive; the platinum complexes showed some activity.

A significant tailoring of terpene amines toward primary, secondary, and tertiary derivatives can be anticipated from both the reaction time and the ammonia concentration. A high excess of ammonia (5/1 NH_3 to isoprene) yields predominantly the primary amines 1–3 (Table III). The low conversion rate can be understood on consideration of the blocking of active sites of the catalyst by excess ammonia. A high isoprene/ammonia ratio does not lead to exclusive formation of the tertiary amine 7, though its amount is enhanced significantly. This can be explained

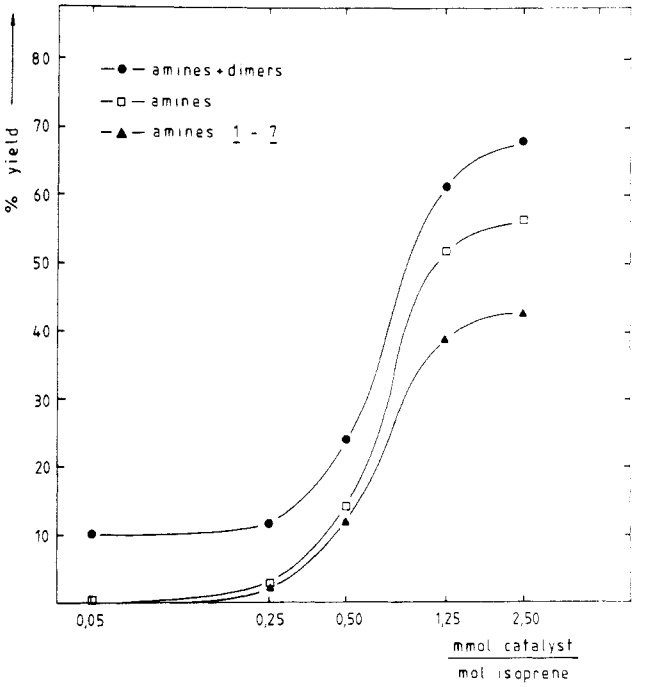


Figure 3. Influence of catalyst concentration on the terpene amine synthesis. Conditions: 1.00–0.01 mmol of $Pd(acac)_2$, 4.00–0.04 mmol of $P(OBu)_3$, 25 mL of CH_3CN, 0.2 mol of isoprene, 0.2 mol of NH_3, temperature 120 °C, reaction time 20 h, stainless-steel autoclave.

by the steric hindrance during attack of a secondary amine on the coordinated isoprene dimer.

The terpene amine formation has been proved to be a consecutive reaction. Primary amines are formed first

(12) M. Meier and F. Basolo, *Inorg. Synth.* 13, 112 (1972).

Table IV. Control of Regioselectivity by Acidic Additives[a]

			product composition by GC, %							
expt	additive	% yield[b]	amines 1-7	1	2	3	4	5	6	7
17		69	63	3	9	5	13	7	12	14
19	CO_2[c]	64	57	4	8	4	12	6	11	12
20	CO_2[c,d]	39	62	20	10	4	9	4	7	8
21	MSA[d]	69	43	11	6	4	8	4	8	2
22	$CHCl_2COOH$	33	43	20	6	3	4	4	4	2

[a] Reaction conditions: 0.5 mmol of $Pd(acac)_2$, 2.0 mmol of $P(OBu)_3$, 25 mL of CH_3CN, 0.2 mol of isoprene, 0.2 mol of NH_3; 5.0 mmol of additive, 120 °C temperature, 20-h reaction time. [b] Quotient of reaction products/isoprene. [c] 1.0 g of CO_2. [d] 100 °C reaction temperature.

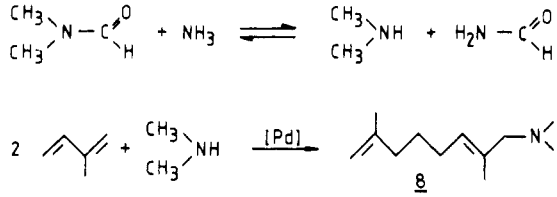
whereas long reaction times favor secondary and tertiary amines. This is shown in Figure 2.

Catalyst Concentration. In homogeneous, transition-metal-catalyzed reactions the catalyst concentration often is of importance. As is shown in Figure 3, low catalyst concentrations yield predominantly isoprene dimers.

Amine formation prevails on starting from 0.5 mmol of catalysts/mol of isoprene terpene. At 1.25 mmol of catalyst/mol of isoprene, turnover numbers of 500 can be obtained. A further increase does not effect the conversion.

It is interesting to notice that a rather high catalyst concentration is necessary to give good selectivities and conversions. This observation is in agreement with our postulated mechanism proposing bimetallic intermediates.

Solvent. The proper choice of a solvent turned out to be very important. Good results were only obtained when aprotic, polar solvents were used. Among these the following order was established: CH_3CN > sulfolane > Me_2SO > t-C_4H_9OH > dimethylacetamide. The highest yield and best selectivity were found in acetonitrile. Solvents possessing an active hydrogen participate in the telomerization. Other polar solvents such as dimethylformamide and acetone may give side reactions; for instance, *N,N*-dimethyl terpene amine 8 was formed in high



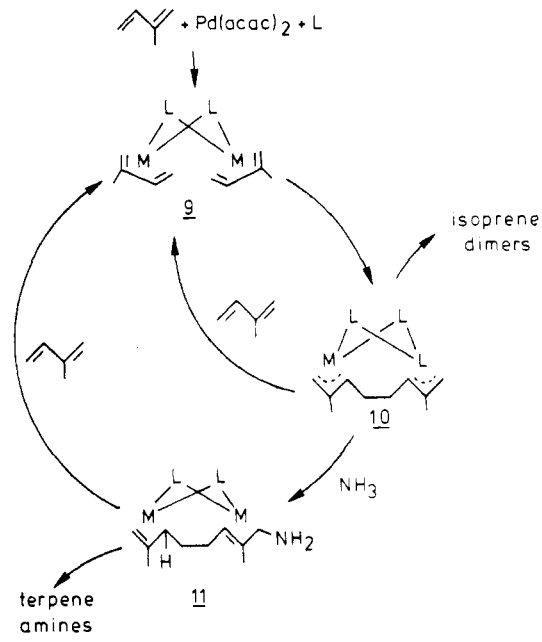
yields from dimethylformamide. Amine 8 was also prepared in high yield and selectivity by the direct palladium-catalyzed telomerization of isoprene with dimethylamine.

The formation of terpene amines has already been reported by Green et al., who used $Pd(COD)_2$ as the catalyst and morpholine as a highly active nucleophile.[13]

Regioselectivity. The formation of terpene amines is a highly regioselective process. Considering the C–C linkage to be possible, one observes only the head–tail and tail–tail couplings, the latter one predominating. This is in agreement with our proposed reaction mechanism discussed in the following section. As is evident from intermediate **10** (Scheme II), the methyl groups show a minimum of steric interactions in this case.

Interestingly, the addition of acids such as $CHCl_2COOH$ directs the C–C coupling toward the head-to-tail product which is formed in up to 20% selectivity. The same selectivity is also observed when CO_2 is used, on lowering the temperature (compare expt 19 and expt 22).

Scheme II



Reaction Mechanism. Although the telomerization of 1,3-dienes has been known since 1967, the mechanism of this reaction remains controversial. The mechanisms, which are based on η^3-allylic palladium complexes as active species are discussed. Mono- and bimolecular η^3-allylpalladium complexes are postulated as intermediates. We favor the bimetallic approach, and Scheme II outlines our proposed reaction path.

The starting step is the coordination of isoprene, giving intermediate **9** which upon C–C linkage yields **10**. Complexes similar to **10** have been isolated.[14-17] The formation of the isoprene dimers can be derived in the cycle elucidated (**9** → **10** → **9**). The terpene amines also can be deduced from intermediate **10** by nucleophilic attack of ammonia. In this way the catalytic cycle is closed via intermediate **11**. In **11** the ammonia can be added at the 1- or 3-position, leading to the described amines. As has been shown by deuterium experiments, the hydrogen always adds on carbon 6 in the C_8 chain.[18] The outlined mechanism is also in agreement with our finding that a high palladium concentration favors the terpene amine formation.

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(18) W. Keim in "Transition Metals in Homogeneous Catalysis", G. N. Schrauzer, Ed., Marcel Dekker Inc., New York, 1971, p 59.

Experimental Section

General Methods. Infrared spectra (neat) were measured on KBr plates with a Perkin-Elmer 577 spectrometer. ^1H NMR spectra were recorded on a 270-MHz instrument (Bruker WH-270) in deuteriochloroform against tetramethylsilane as an internal standard. The ^1H NMR spectrum of 8 as well as spin–spin decoupling experiments were carried out on a 90-MHz instrument (Varian EM-390). Mass spectra were recorded on a Varian MAT 112S GC/MS system in the EI mode (70 eV, 0.7 mA).

Reagents. The solvents were commercially available, purified by distillation, and stored under argon. Dry ammonia and carbon dioxide were used without further purification. the phosphorous ligands were commercially available. $Pd(acac)_2$ was prepared from $PdCl_2$ by a modified procedure similar to that described by Grinberg.[19] The $M[P(OEt)_3]_4$ complexes were prepared from $NiCl_2 \cdot 6H_2O$, K_2PdCl_4, and K_2PtCl_4, respectively, as reported by Meier and Basolo.[12]

Preparation of $Pd[P(OC_4H_9)_3]_4$. This complex was prepared in a manner analogous to the method of Meier and Basolo.[12] A dark red solution of 3.3 g of K_2PdCl_4 (0.01 mol) in 30 mL of water was added to 12.5 g of $P(OC_4H_9)_3$ (0.05 mol) in 30 mL of methanol under cooling in an ice bath. A few drops of methanol were added until the yellow mixture became homogeneous, and under further cooling and stirring 2.1 mL of diethylamine was introduced by a syringe. The mixture decolored, and an oil precipitated. After removal of methanol, the aqueous phase was separated and the remaining oil extracted several times with water. The excess of ligand was removed under high vacuum, and $Pd[P(OC_4H_9)_3]_4$ resulted as a colorless, air-sensitive oil. Anal. Calcd for $C_{48}H_{108}O_{12}P_4Pd$: C, 52.05; H, 9.83; P, 11.19; Pd, 9.61. Found: C, 51.04; H, 9.98; P, 11.4; Pd, 9.6.

General Procedure for the Reaction of Ammonia and Isoprene. All operations except the workup of the reaction products were carried out under argon. For the catalytic telomerization 0.5 mmol of catalyst (in 25 mL of CH_3CN), 0.2 mol of isoprene, and the ligand were stirred in a Schlenk tube. (The acidic cocatalysts, added in some experiments, were also introduced at this point.) The homogeneous solution was transferred to a magnetically stirred 75-mL stainless-steel autoclave.[20] Pressurized NH_3 (0.2 mol) and if noted 1.0 g of pressurized CO_2 were added. The autoclave was then transferred into a magnetically stirred oil bath. After 20 h the autoclave was cooled, the remaining pressure released, and the reaction mixture extracted with 30 mL of water in a separating funnel. The organic layer was filtered to remove palladium particles, and the reaction products were isolated by evaporating the solvent and unreacted isoprene at 30 °C (20 mm). Product composition was determined by GC analysis on a packed column (2 m, Carbowax 20M). Sensitivity factors were determined by the method of Kaiser.[21] A detailed description of this general procedure for one example is given below.

Terpene Amine Synthesis with the $Pd(acac)_2/P(OC_4H_9)_3$ Catalyst System. In a 150-mL Schlenk tube was dissolved 0.5 mmol of $Pd(acac)_2$ in 25 mL of CH_3CN, and 0.2 mol of isoprene was added. To the yellow solution was added 2.0 mmol of $P(OC_4H_9)_3$ by a syringe. After a few minutes the homogeneous solution turned colorless. The air-sensitive solution was transferred to a 75-mL stainless-steel autoclave, and 0.2 mol of pressurized ammonia was added. The autoclave was heated for 20 h in a magnetically stirred oil bath to 120 °C. After the mixture cooled, the excess of ammonia was released, and the two-phase reaction mixture was extracted with 30 mL of H_2O. The organic layer was filtered to remove traces of palladium metal. After evaporation of isoprene and acetonitrile 9.41 g of a yellow oil was obtained (yield 69%). The GC analysis gave 17% of isoprene dimers, mainly 2,7-dimethyl-1,3,7-octatriene and the Diels–Alder products, 3% 3,7-dimethyl-1,7-octadien-3-amine (α-linalylamine, 1), 9% 2,7-dimethyl-1,7-octadien-3-amine (2), 5% 2,7-dimethyl-2,7-octadien-1-amine (3), 13% (2,7-dimethyl-1,7-octadien-3-yl)(2,7-dimethyl-2,7-octadien-1-yl)amine (4), 7% [(*E*)-2,7-dimethyl-2,7-octadien-1-yl][(*Z*)-2,7-dimethyl-2,7-dimethyl-2,7-octadien-1-yl)]amine (5), 12% bis(2,7-dimethyl-2,7-octadien-1-yl)amine (6), and 14% tris(2,7-dimethyl-2,7-octadien-1-yl)amine (7).

For isolation of the terpene amines the reaction was scaled up by a factor of 10 and was carried out in a 1-L stainless-steel autoclave. The reaction mixture was separated into three fractions by distillation: bp 80 °C (20 mm)–115 °C (8 mm) (primary amines), 90 °C (0.08 mm)–150 °C (0.001 mm) (secondary amines), and 130–160 °C (0.0001 mm) (tertiary amines). Separation of the individual terpene amines was carried out by preparative GC on a 2 m × 2 cm collumn filled with 30% Carbowax 20M on Chromosorb P-NAW (30/60-mesh) at 180–220 °C (inlet 350 °C).

3,7-Dimethyl-1,7-octadien-3-amine (α-linalylamine, 1): IR (neat) 3370, 3290 (NH_2), 1648 (C=C), 995 ($CH=CH_2$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (s, 3 H), 1.33 (m, 2 H), 1.40 (m, 4 H), 1.70 (m, 3 H), 1.99 (m, 2 H), 4.67 (m, 2 H), 4.98 (d, J = 10 Hz, 1 H), 5.08 (d, J = 17 Hz, 1 H), 5.87 (dd, J = 10, 17 Hz, 1 H); mass spectrum, m/e (relative intensity) 138 (1.0, $M^+ \cdot - 15$), 70 (100), 30 (10). Anal. Calcd for $C_{10}H_{19}N$: C, 78.36; H, 12.50; N, 9.14. Found: C, 78.19; H, 12.49; N, 9.10.

2,7-Dimethyl-1,7-octadien-3-amine (2): IR (neat) 3375, 3300 (NH_2), 1646 (C=C), 886 ($C=CH_2$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5 (m, 2 H), 1.43 (m, 4 H), 1.70 (m, 6 H), 2.03 (m, 2 H), 3.36 (m, 1 H), 4.68 (m, 2 H), 4.80 (m, 2 H); mass spectrum, m/e (relative intensity) 138 (0.7, $M^+ \cdot - 15$), 70 (100), 30 (8). Anal. Calcd for $C_{10}H_{19}N$: C, 78.36; H, 12.50; N, 9.14. Found: C, 78.43; H, 12.44; N, 9.22.

2,7-Dimethyl-2,7-octadien-1-amine (3): IR (neat) 3380, 3300 (NH_2), 1646 (C=C), 885 ($C=CH_2$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (m, 2 H), 1.50 (m, 2 H), 1.64 (m, 3 H), 1.72 (m, 3 H), 2.03 (m, 4 H), 3.28 (m, 2 H), 5.31 (t, J = 6 Hz, 1 H); mass spectrum, m/e (relative intensity) 138 (7.4, $M^+ \cdot - 15$), 136 (6.2, $M^+ \cdot - 17$), 70 (100), 30 (74). Anal. Calcd for $C_{10}H_{19}N$: C, 78.36; H, 12.50; N 9.14. Found: C, 78.14; H, 12.50; N, 8.89.

(2,7-Dimethyl-1,7-octadien-3-yl)(2,7-dimethyl-2,7-octadien-1-yl)amine (4): IR (neat) 3340 (NH), 1648 (C=C), 886 ($C=CH_2$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (m, 1 H), 1.41 (m, 4 H), 1.48 (m, 2 H), 1.62 (m, 6 H), 1.68 (m, 3 H), 1.70 (m, 3 H), 2.00 (m, 6 H), 2.97 (m, 3 H), 4.67 (m, 4 H), 4.82 (m, 2 H), 5.28 (t, J = 7 Hz, 1 H); mass spectrum, m/e (relative intensity) 289 (1.1, $M^+ \cdot$), 206 (51), 81 (69), 70 (100), 30 (11). Anal. Calcd for $C_{20}H_{35}N$: C, 82.97; H, 12.19; N, 4.84. Found: C, 83.01; H, 12.33; N, 4.99.

[(*E*)-2,7-Dimethyl-2,7-octadien-1-yl][(*Z*)-2,7-dimethyl-2,7-octadien-1-yl]amine (5): IR (neat) 3340 (NH), 1648 (C=C), 885 ($C=CH_2$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (m, 1 H), 1.47 (m, 2 H), 1.50 (m, 2 H), 1.64 (m, 3 H), 1.60 (m, 6 H), 1.76 (m, 3 H), 2.02 (m, 8 H), 3.12 (m, 4 H), 4.67 (m, 4 H), 5.28 (t, J = 7 Hz, 1 H), 5.31 (t, J = 8 Hz, 1 H); mass spectrum, m/e (relative intensity) 289 (4.8, $M^+ \cdot$), 206 (5.0), 81 (100), 70 (52), 30 (49). Anal. Calcd for $C_{20}H_{35}N$: C, 82.97; H, 12.19; N, 4.84. Found: C, 82.59; H, 11.96; N, 4.75.

Bis(2,7-dimethyl-2,7-octadien-1-yl)amine (6): IR (neat) 3330 (NH), 1648 (C=C), 885 ($C=CH_2$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (m, 1 H), 1.50 (m, 4 H), 1.64 (m, 6 H), 1.70 (m, 6 H), 2.02 (m, 8 H), 3.09 (m, 4 H), 4.69 (m, 4 H), 5.31 (t, J = 7 Hz, 2 H); mass spectrum, m/e (relative intensity) 289 (2.8, $M^+ \cdot$), 206 (11) 81 (100), 70 (45), 30 (57). Anal. Calcd for $C_{20}H_{35}N$: C, 82.97; H, 12.19; N, 4.84. Found: C, 82.48; H, 11.97; N, 4.76.

Tris(2,7-dimethyl-2,7-octadien-1-yl)amine (7): IR (neat) 3075 (C=CH), 1648 (C=C), 886 ($C=CH_2$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (m, 6 H), 1.62 (m, 9 H), 1.72 (m, 9 H), 2.02 (m, 12 H), 2.80 (m, 6 H), 4.71 (m, 6 H), 5.32 (t, J = 7 Hz, 3 H); mass spectrum, m/e (relative intensity) 425 (3.8, $M^+ \cdot$), 342 (14), 302 (26), 81 (100), 70 (6), 30 (25). Anal. Calcd for $C_{30}H_{51}N$: C, 84.63; H, 12.08, N, 3.29. Found: C, 84.69; H, 12.30; N, 3.40.

Preparation of *N,N*,2,7-Tetramethyl-2,7-octadien-1-amine. In a manner analogous to the outlined general procedure, 0.5 mmol of $Pd(acac)_2$, 2.0 mol of $P(OC_4H_9)_3$, 25 mL of CH_3CN, 0.2 mol of isoprene, and 0.1 mol of dimethylamine were reacted for 20 h at 100 °C in a 75-mL stainless-steel autoclave. After extraction with 30 mL of water and removal of the solvent and excess isoprene at reduced pressure, a yellow oil (17.0 g, 92% yield) was obtained, containing 69% of 8 (GC). Amine 8 was isolated by distillation as a colorless liquid [bp 95.5–96.0 °C (13 mm)] and proved to be identical with the compound obtained when isoprene was reacted

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with ammonia in DMF in the presence of CO_2: IR (neat) 3075 (C=CH), 1648 (C=C), 884 (C=CH_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (m, 2 H), 1.64 (m, 3 H), 1.70 (m, 3 H), 2.00 (m, 4 H), 2.19 (s, 6 H), 2.75 (m, 2 H), 4.69 (m, 2 H), 5.32 (t, J = 7 Hz, 1 H); mass spectrum, m/e (relative intensity) 181 (2.1, $M^{+\cdot}$), 98 (10), 58 (100), 44 (33), 30 (7). Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.72. Found: C, 79.66; H, 12.74; N, 7.76.

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Registry No. 1, 77984-56-6; 2, 77984-57-7; 3, 77984-58-8; 4, 77984-59-9; 5, 77984-60-2; 6, 77984-61-3; 7, 77984-62-4; 8, 77984-63-5; ammonia, 7664-41-7; isoprene, 78-79-5; 2,7-dimethyl-1,3,7-octatriene, 36638-38-7; dimethylamine, 124-40-3; K_2PdCl_4, 10025-98-6; $P(OC_4H_9)_3$, 102-85-2; $Pd[P(OC_4H_9)_3]_4$, 77984-64-6; $P(OCH_3)_3$, 121-45-9; $P(OC_2H_5)_3$, 122-52-1; $P(O\text{-}i\text{-}C_3H_7)_3$, 116-17-6; $P(OCH_2CH{=}CH_2)_3$, 102-84-1; $P(OC_6H_5)_3$, 101-02-0; $P(C_4H_9)_3$, 998-40-3; $P(c\text{-}C_6H_{11})_3$, 15205-58-0; $P(C_6H_5)_3$, 603-35-0; $Ni[P(OC_2H_5)_3]_4$, 14839-39-5; $Pd[P(OC_2H_5)_3]_4$, 38266-18-1; $Pd[Ph_3P)_4$, 14221-01-3; $Pt[P(OC_2H_5)_3]_4$, 23066-15-1; $Pt[PPh_3]_4$, 14221-02-4; $Pd(acac)_2$, 14024-61-4.

Supplementary Material Available: IR spectra, ^1H NMR spectra, and mass spectra of the eight amines prepared (20 pages). Ordering information is given on any current masthead page.

Metal Catalysis in Organic Reactions. 12.[1] Asymmetric Induction Phenomena in the Isomerization of Racemic 1-Alkenes by Chiral Aluminum Solvate-Nickel Systems

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The isomerization of some racemic 1-alkenes in the presence of chiral amine-triisobutylaluminum solvate-bis(*N*-methylsalicylaldimine)nickel systems has been studied. The susceptibility to isomerization of the alkenes was found to be related to their structure and in particular to the nature of the amine used. However (*E*)-2-alkenes had been recovered as main products both in the absence and in the presence of the amine in the catalytic system. In most of the cases investigated, asymmetric induction phenomena take place, both in the isomerization reaction and in the competitive displacement reaction. The nature of the active species is discussed, and reasonable reaction paths are presented.

Recently we have reported the occurrence of chiral discriminating processes in the isomerization of racemic 1-alkenes by an optically active amine-*i*-Bu_3Al solvate-nickel system.[1] In continuing our research, we have now extended the investigations to elucidate some aspects of the isomerization of 1-alkenes by catalytic systems obtained through interaction of an *i*-Bu_3Al chiral solvate with bis(*N*-methylsalicylaldimine)nickel. The present paper deals therefore with some features of the dynamics and the stereochemistry of the reaction, along with a mechanistic approach to the mode of the action of the catalytic system.

Experimental Section

Boiling points are uncorrected. GLC analyses were performed on Perkin-Elmer F 30 and 3920B instruments (flame-ionization detectors; 200 × 0.30 cm columns packed with 5% silicone SE 301 on 80/100-mesh Chromosorb A at 40–200 °C, 8% Carbowax 20M + 2% KOH on 80/100-mesh Chromosorb W at 40–200 °C, 10% $AgNO_3$ + 30% glycerol on 80/100-mesh Chromosorb W DMCS at 20–80 °C, and 10% $AgNO_3$ + 30% ethylene glycol on 80/100-mesh Chromosorb P at 20–50 °C; nitrogen flow rate of 12–18 mL min^{-1}).

Preparative GLC was carried out on a Perkin-Elmer F 21 chromatograph using 300 × 0.80 columns filled with 8% Carbowax + 2% KOH on 80/100-mesh Chromosorb P (CwKOH) and 10% Ag NO_3 + 30% glycerol on 80/100-mesh Chromosorb W DMCS (Ag-G).

Spectral measurements were determined with the following instruments: IR, Perkin-Elmer Model 225; NMR, Varian XL A 100 at 100 MHz; mass spectra, Varian MAT CH7. Optical rotations were measured with a Perkin-Elmer 142 polarimeter; unless otherwise specified, rotations refer to pure liquid.

General Reagents. Triisobutylaluminum (Fluka A. G., Co., Buchs) and tris[(*R*)-2,3-dimethylbutyl]aluminum[2] were carefully redistilled under nitrogen and stored in sealed capillary glass vials in weighed amounts. Bis(*N*-methylsalicylaldimine)nickel [Ni(mesal)$_2$] and (-)-(DIOP)$NiCl_2$ were prepared and purified as reported elsewhere.[3,4] *N,N*-Dimethylmenthylamine (DMMA) [bp 92–93 °C (18 mmHg), α^{25}_D -46.59° (l = 1)], *N,N*-dimethylbornylamine (DMBA) [bp 54 °C (0.8 mmHg), $[\alpha]^{25}_D$ +24.94° (ethanol)], (*R*)-*N,N*-dimethyl-1-phenylethylamine (DMPEA) [bp 92–94 °C (30 mmHg), $[\alpha]^{25}_D$ +67.68° (heptane)] were prepared by the corresponding amines[5-7] by using a general method[8] for the methylation of amines. (L)-Sparteine was prepared from sparteine sulfate (Merck) according to a previously reported procedure.[9]

(*RS*)-4-Methyl-1-hexene was prepared according to established procedures.[10] (*R*)-4-Phenyl-1-hexene (bp 90–91 °C (18 mmHg), $[\alpha]^{25}_D$ -8.68°)[11] and (*R*)-4-phenyl-5-methyl-1-hexene (bp 97–98

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