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ON THE MECHANISM OF THE NICKEL-CATALYSED REGIOSELECTIVE CYCLODIMERIZATION OF ISOPRENE

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Abstract—A study of various Ni-ligand catalysed oligomerizations of isoprene has shown that with π-acidic P ligands the selectivity to cyclodimers amount to 97%. A new type of ligand is introduced, viz. fluoroalkyl phosphites having π-acceptor properties comparable to those of, e.g. PCl_3. With tris(hexafluoroisopropyl) phosphite the main product is 1,4-dimethyl-4-vinylcyclohexene. A detailed explanation based on a two-step mechanism is given. As to the first step, for a series of ligands having similar steric properties the changes in product distribution as a function of the electronic ligand parameter are explained in terms of a gradual change in HOMO-LUMO interactions between Ni and the olefins, with strong π-acidic ligands promoting the head-to-head coupling of the isoprene molecules. The second step, involving reductive elimination of a cyclodimer from the metal, shows an increasing selectivity towards substituted cyclohexenes for the head-to-head and tail-to-tail intermediates with increasing π-acidity of the ligand. The qualitative orbital treatment presented as an explanation is also applicable to reactions found for other metallacyclopentanes.

Varying the ligands of a metal catalyst has become a common procedure to steer a catalytic process occurring at the metal centre to higher rates and selectivities of the reactions desired. Numerous examples are known from homogeneous catalysis where subtle changes in the surrounding ligands have enormous effects on the characteristics of the catalysis, and there is hardly any reaction that is not affected: the result of changing the ligand is often as dramatic as replacing the metal itself. An understanding of these phenomena requires detailed information of the catalytic process and an extensive knowledge of the properties of the ligands, preferably obtained on complexes representative of those postulated for the reaction studied. The ranking of the ligands according to some property of a complex or a reaction has been the subject of numerous studies and several series of ligands in the order of strength have been published[1,2] (*trans* effect, *trans* influence, as based on IR frequencies, substitution reaction rates, NMR chemical shifts, NMR coupling constants). At a later stage the steric properties of the ligands were also recognized as being of great importance. The steric properties were expressed in terms of the "cone angle", a concept introduced by Tolman and representing the angle of the cone enclosing the van der Waals radii of the outermost atoms of the P ligand.[3] With these concepts in hand one might be tempted to think that satisfactory explanations can be given for the stereo-selectivities and rates observed for homogeneous catalytic reactions under the influence of various ligands, particularly if the range of ligands were to be restricted to P ligands. However, despite the recognized importance and the vast amount of data available from organometallic chemistry, there is no clear-cut example of a homogeneous catalytic reaction where the steric and electronic factors have been sufficiently delineated and successfully used to explain the product distribution, let alone to predict it. It would seem that mainly noncatalytic reactions or equilibria can be accounted and that catalytic processes are as yet too complicated to be fully understood. In the catalytic reactions studied in detail often one factor predominates (e.g. the steric factor in the nickel-catalysed reaction of norbornadiene and acrylonitrile;[4] and in the nickel-catalysed propene dimerization;[5] the electronic factor in the hydrogenation with $RhClL_3$[6] and in the Rh-catalysed hydroformylation[7]). However, there are many examples (see Ref. 1) where the situation is less clear and explanations tend to be speculative. In view of the correlation between steric and electronic properties a clear separation of the two is not realistic and it may seem that a full understanding can only be obtained by calculations of energies as a function of atomic distances. This being impossible one might restrict oneself to series where one factor is kept more or less constant.

We have studied the Ni-catalysed cyclodimerization of isoprene, which has been reported on before.[8,9] A variety of isomers is formed in this reaction. Usually, the regioselectivity or stereoselectivity in catalytic systems is thought to be related to the steric properties of the ligand,[4] and when electronic factors are considered such as in the Ni-catalysed butadiene cyclodimerization[10] their influence is noted but a convincing explanation is lacking.[11] It is obvious that even when steric factors can safely be neglected the interpretation of the electronic influence will not be a simple one based on charge distributions only. Up to now bonding interactions in organometallic chemistry have been successfully expressed in terms of molecular orbitals both in a qualitative and in a quantitative manner. The recent applications of molecular orbital theory for the explanation of many aspects of chemical reactivity in organic chemistry[12] (known as the frontier orbital theory by Fukui) may inspire[10] a similar approach in homogeneous catalysis. So far the frontier orbital concept has been applied to a very few straightforward one-step reactions. In the following we will give an illustration of the many complications involved in a catalysed system, even though the cyclodimerization of dienes on Ni catalysts has been studied in great detail over the past decade.[8-11, 13-18]

RESULTS

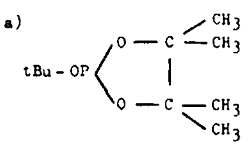
Isoprene, when contacted with the Ni-ligand catalysts, gave rise to a variety of products such as oligomers,

Table 1. Selectivities to various products in ligand-nickel catalysed oligomerizations of isoprene under standard conditions (see Experimental)

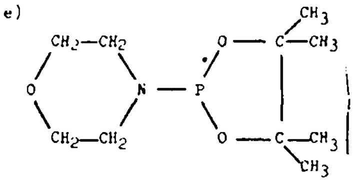
Ligand number	Ligand	χ	θ	Time, h	Isoprene conversion, %	selectivity (%) to									% of 1,5-DMCOD on total DMCOD	Remarks
						Linear trimer	Cyclic trimer	Cyclic dimer	1,4-DMVCH	1,6-DMCOD	2,4-Limonene	1,5-DMCOD	1,4-Limonene	2,4-DMVCH		
L-1	$P(t\text{-}Bu)_3$	0	182	20	93	6.6	18.8	40.7	11.6	2.8	8.0	5.7	12.5		67	
L-2	$P(n\text{-}Bu)_3$	5.2	132	18	82	22.7	8.8	37.4	7.8	9.0	4.9	7.3	8.4		45	
L-3	$P(CH_2\phi)_3$	10.5	165	23	98	19.9	18.4	21.2	4.5	4.2	2.8	4.9	4.9		54	
L-4	$P\phi_3$	12.9	145	17	99	20.4	18.3	27.1	4.2	5.0	2.9	11.2	3.8		69	
L-5	$P(OCH_3)_3$	23.3	107	22	92	11.0	20.0	22.4	2.8	3.9	4.3	7.0	4.3		64	
L-6	$P(OnBu)_3$	19.5	109	19	58	25.2	20.3	31.4	4.5	4.9	6.0	8.3	7.7		63	
L-7	$P(OiPr)_3$	18.9	130	21	99	7.4	15.9	73.9	13.2	21.4	5.5	26.2	7.6		55	
L-8	$P(OsBu)_3$	18.9	131	6	70	11.3	9.9	75.4	15.2	16.9	5.9	30.1	7.1	0.2	64	
L-9	$P(OCH_2\phi)_3$	27	140	19	98	14.3	18.1	13.5	1.5	22.0	1.5	5.0	3.0	0.1	69	
L-10	$P(OCH_2)_3CCH_3$	31.2	101	23	99	6.6	45.0	14.9	1.8	2.2	2.2	5.8	2.8	-	72	
L-11	a)	24^b	140	19	98	9.1	8.3	67.6	7.2	18.6	8.4	30.3	3.1		62	
L-12	$P(OC_6H_4R)_3$ R = H	29.1	128	5	74	5.5	20.8	72.7	7.2	13.0	2.3	46.2	4.0		78	
L-13	do R = p-Cl	34.5	128	21	93	5.3	21.8	73.0	9.3	10.8	2.0	45.9	5.0		81	
L-14	do R = $o\text{-}CH_3$	28.0	141	3	98	5.5	10.3	84.2	14.2	12.2	1.4	52.3	4.0		81	
L-15	do R = $o\text{-}\phi$	28.9	152	3	97	4.1	7.2	85.7	16.7	11.2	1.2	51.0	5.5		82	
L-16	do R = p-CN	36.6	128	22	50	11.2	15.2	44.0	6.9	10.2	12.6	6.2	7.7		81	
L-17	do R = o-F	32^b	132	1	99	2.5	11.9	80.5	16.7	13.0	1.3	43.5	6.0		77	at 115 °C
L-18	do R = o-tBu	28.8	175	6	50	3.4	11	45	13.8	3.4	4.9	14.6	8.3		81	at 115 °C 0.5 mmol of L
L-19	do R = i-Pr	28.5	148	3	65	8.7	9.5	78.6	14.5	11.5	2.0	46.3	4.3		80	at 110 °C
L-20	$P(OCH_2CF_3)_3$	39.3^c	110	4.5	50	42.2	23.0	27.8	6.1	4.3	2.4	12.3	2.6	0.1	74	at 120 °C 0.5 mmol of L
L-21	$P(OCHCF_3CH_3)_3$	39.0^c	130	3	85	5.1	11.3	78.8	19.7	7.5	3.2	42.2	6.2	0.1	85	
L-22	$P(OCHC_2F_5CH_3)_3$	40.0^c	130	2.5	87	6.2	5.5	81.8	29.7	6.2	3.5	35.0	7.4	0.2	85	
L-23	$P(OCHCF_3\phi)_3$	36.9^c	150^b	5	55	4.3	8.4	86.7	22.7	5.2	4.9	46.6	7.3	0.1	90	
L-24	$P(O\text{-}iC_3HF_6)_3$	51.3^c	130	0.7	100	1.8	2.3	97.4	60.1	1.0	6.35	18.8	11.5	0.1	95	0.75 mmol of L

L-25	$P(O\phi)_2(OiC_3HF_6)$	36.5[d]	129	1.8	100	1.1	8.9	90.0	18.7	7.2	1.7	56.3	6.2		87	
L-26	$P(O\phi)(OiC_3F_6H)_2$	43.9[d]	129	0.9	96	1.0	3.1	96	38.0	3.3	3.4	42.2	8.4		93	
L-27	$P(N(CH_3)_2)_3$	5.8	157	6.8	60	31.8	12.3	35.0	8.5	5.6	5.4	4.6	10.4	0.5	45	
L-28	$P\phi_2(O\phi)$	18.5	139[b]	23	99	7.1	19.3	37.2	5.8	10.4	4.0	12.2	5.1		54	
L-29	$P\phi(O\phi)_2$	23.7	132[b]	20	96	6.3	14.2	79.4	7.5	18.4	4.8	43.0	5.6		70	
L-30	$P(NC_2H_4OC_2H_4)_3$	5.7	130[b]	4	30	36.3	14	34.3								
L-31	e)	21[b]	130[b]	5	75	7.2	3.6	81.2	9.6	19.9	13.7	30.4	6.7		60	at 120 °C with 1 mmol of L

a)



e)



b) estimated

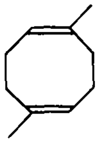
c) this work, determined according to published procedure[3]

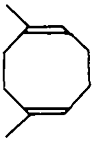
d) this work, calculated

$P(OR)_3$ - Alkyl phosphites prepared according to method A.					
Ligand number	R =	Boiling point, °C/mm Hg	Yield, %	^1H NMR δ(ppm) in $CDCl_3$	^{31}P NMR δ(ppm) from H_3PO_4
L - 20	CH_2CF_3	63/6	90	4.23 q	-143.6
L - 24	$CH(CF_3)_2$	70/35	90	4.36 m	-139.7
L - 23	$CH(CF_3)C_6H_5$	152/0.1	90	5.32m(1H)7.34 (5H)	
L - 22	$CH(CH_3)C_2F_5$	90/15	90	4.7 m(1H)1.44d(3H)	
L - 21	$CH(CH_3)CF_3$	95/40	65	4.74m(1H)1.44d(3H)	
L - 3	s - Bu	00/3	70		

$P(O\phi)_3$ phosphites prepared according to method B.				
Ligand number	R =	Melting point, °C or Boiling point, °C/mm Hg	Yield, %	^{31}P NMR
L - 15	o-ϕ	mp.93-95	40	
L - 16	p-CN	mp.98-120	80	
L - 17	o-F	143/0.5	80	
L - 18	o-Bu^t	~190/0.05	90	-142.0
L = 19	o-Pr^i	187/0.15	80	-130.6

linear and cyclic trimers and cyclic dimers. Of the cyclic dimers the following isomers were formed†:


1
1,5-DMCOD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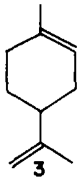
1,6-DMCOD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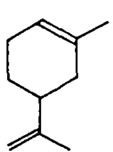
1,4-LiM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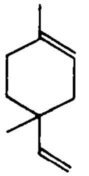
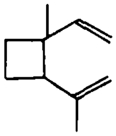
2,4-LiM


5
1,4-DMVCH


6
DMVCB

The catalyst was formed *in situ* from bis(acetylacetonato) nickel and triethylaluminium (molar ratio 1:6) or use was made of bis(1,5-cyclooctadiene)nickel, together with the ligand (ligand: Ni = 1:3). The Ni to isoprene ratio amounted to 1:1000. For practical purposes the solvent consisted of a mixture of THF, isooctane and N-methylpyrrolidone though the main solvent was isoprene or products formed from it. A large number of P ligands were tested with the aim of obtaining a catalyst system that would give 1,5-DMCOD in high purity or other desired products such as 1,4-DMVCH. The results obtained for a few ligands, though reported previously,[8] have been reproduced here for convenience as selectivities to products in Table 1. The results are also graphically represented in the form of plots showing the selectivities as a function of ligand parameters. The ligand parameters used were taken from Tolman's work[1] or they were determined experimentally. The experimental determination was carried out for a newly used group of ligands, viz. that of fluoro-substituted alkyl phosphites. The steric parameter, the cone angle θ, is defined as stated in the Introduction, and was obtained by Tolman via measurements on CPK models or experimentally by comparison of equilibrium constants for ligand dissociation reactions. The electronic parameter χ‡ is derived from the A_1 IR frequency of the CO mode in $Ni(CO_3)L$ which was shown to be[2] a reliable measure of the electronic properties of L because steric repulsions in this complex are negligible with most ligands. A low χ-value (0) means a strong donor, while high χ-values (60) stand for strong electron-acceptor-type ligands. For an extensive description of these concepts see Ref. 1. The χ-values and θ-values are collected in Table 1.

In Fig. 1 we have plotted the selectivity of converted isoprene to the total amount of the various cyclodimers versus the electronic parameter χ. Figure 1 also shows the selectivities to the sum of 1,5- and 1,6-DMCOD, and the relative amount (in %) of 1,5-DMCOD on the total amount of DMCOD. In Fig. 2 the selectivities to cyclodimer are plotted against the cone angle θ of the ligands. Figure 3 reprsents the distribution of cyclodimers, expressed by means of the various coupling modes: isoprene molecules can be linked together via two C-1 atoms (head-to-head), viz. a C-1 and a C-4 atom (head-to-tail), or via two C-4 atoms (tail-to-tail). These modes correspond to, respectively, the amounts of 1,4-DMVCH, 1,5-DMCOD + 1,4-LiM and 2,4-LiM. It remains undecided to which coupling mode the formation of 1,6-DMCOD must be ascribed. The amount of 1,4LiM is fairly constant for the ligands plotted (7–12%); head-to-tail mainly represents 1,5-DMCOD.

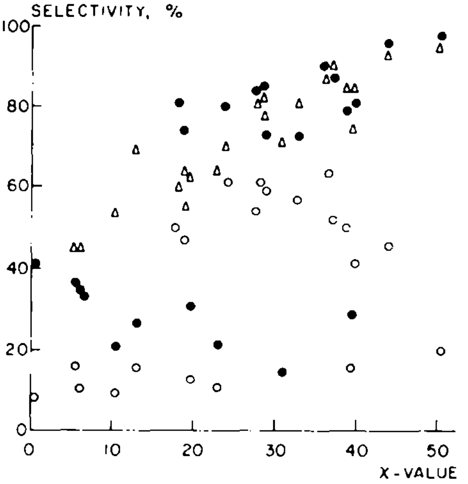


Fig. 1. Selectivities of the nickel ligand-catalysed dimerization of isoprene versus χ-value of the ligand. For conditions, see Experimental: ●, total cyclodimers, ○, total DMCOD, Δ%, 1,5-isomer of DMCOD on total DMCOD.

DISCUSSION OF OBSERVED TERMS

From Fig. 1 it is seen that the selectivity to cyclodimers increases with the χ-value of the ligand. Figure 2 shows that high selectivities to cyclodimers are obtained at θ-values between 125° and 155°. We have confined ourselves to a comparison of the selectivities to the compounds mentioned and we have not studied the rates of formation. The selectivities can be a reliable measure

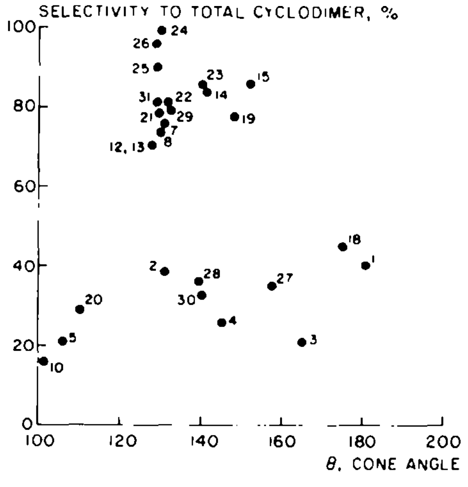


Fig. 2. The selectivity to total cyclodimer vs the cone angle of the ligand (The numbers indicate the ligand numbers).

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†In contrast to other workers we observed the formation of two "limonene" isomers, which are mentioned separately.

‡For χ we have used throughout this work $\chi = \sum_{i=1}^{3} \chi_i$, (with χ_i as defined by Tolman.[1])

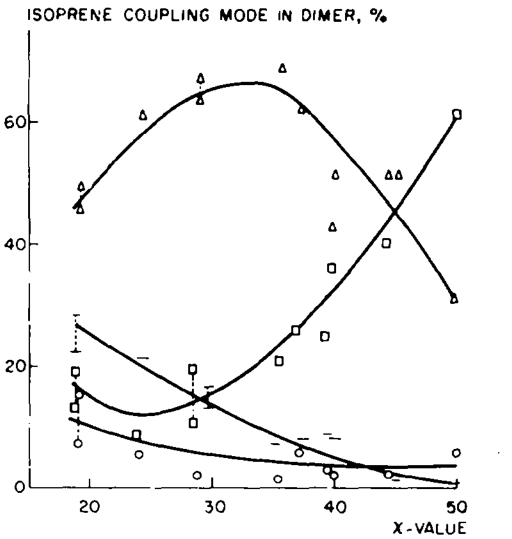


Fig. 3. Isoprene coupling mode in dimer versus χ-value. △, head-to-tail (1,5-DMCOD + 1,4-LiM); □, head-to-head (1,4-DMVCH); ○, tail-to-tail (2,4-LiM); —, both ○ and □ (1,6-DMCOD).

of the individual rates if unexpected side reactions due to impurities may be neglected. Such a neglect is not allowed when ligand decomposition occurs or when small amounts of basic impurities[17] are present in a system that is not very reactive. It was found that generally the overall rate increases with increasing χ-value, as can be seen from the total conversions and reaction times (Table 1).

Figure 1 indicates that there is very little correlation between the selectivity to cyclodimer and the χ-value, although there is a conglomeration of data points at 80% and χ-values of 27–40 which all relate to arylphosphites. That the dimer selectivities indeed show a rather irregular pattern may be seen at $\chi = 19$, 30 and 39 with dimer contents ranging from 30 to 81%, 15 to 85% and 28 to 81%, respectively. Similarly wide-spread ranges are observed for DMCOD. However, if we look at Fig. 2, where the dimer selectivities are plotted versus the cone angle, it is seen that at χ-values > 15 all low dimer selectivities correspond to ligands with cone angles < 125° and > 152°, (except for ligand L-28, $\Theta = 139°$). For all the ligands having a cone angle within this range a steady increase to cyclodimer is noted, with a concomitant decrease in selectivity to oligomers, linear trimers, and cyclic trimers. The formations of oligomer and linear trimers requires the shift of an H atom, which may well be catalysed by a base, and therefore it is not unexpected that basic systems (low χ-values) produce large amounts of these products. Furthermore small amounts of base impurities may catalyse this reaction.[17]

Figure 1 also shows that there is an increase in 1,5-DMCOD content of DMCOD with increasing χ-value, though the points form a band rather than a single line. The observations that up to χ-values of 33, and cone angles between 125 and 152°, an increasing χ-value leads to a higher dimer content, a higher DMCOD content and a higher purity of 1,5-DMCOD constituted the very incentives for the synthesis of the fluoro containing alkyl phosphites. The χ-values of several of them were very high indeed.

The number of ligands with χ-values > 33 is limited and most of them are too reactive with respect to the reactants and/or products (e.g. PCl_3, $\chi = 44.4$; PF_3, $\chi = 54.6$; $P(CF_3)_3 = 58.8$). Fluoroalkyl phosphites therefore represent an easily accessible class of ligands with a variety of cone angles some of which differ ($\chi = 33$–51) as much from common phosphites ($\chi = 18$–33) as phosphites from phosphines ($\chi = 0$–12).

The expectations with respect to hexafluoroisopropyl phosphite are only partly fulfilled; indeed a very pure 1,5-DMOCD is formed, and neglible amounts of trimers are produced, but the yield of DMCOD is rather low (20% at 105° under the present conditions). At χ-values > 35 the yield in 1,4-DMVCH starts to increase at the expense of DMCOD, reaching a maximum of 60% at $\chi = 51$. This is shown in Fig. 3 (note that this represents the distribution of dimers, i.e. total dimer = 100%). The "unfortunate" behaviour at $\chi > 35$ is also reflected in the selectivity to head-to-tail dimer, which is mainly 1,5-DMCOD since 1,4-LiM invariably represents some 10% of the product. At low χ-values (~ 20) there is almost no preference for any coupling mode and if the 1,6-DMCOD part which can be attributed to both the head-to-head and the tail-to-tail mode is distributed evenly over those two modes a more or less statistical coupling (50:25:25) is obtained. Figure 3 only contains the data for reactions with dimer selectivities > 70% since the coupling modes have not been studied for the other products formed.

Before concentrating exclusively on the systems with high dimer selectivities we will pay some attention to the few ligands that have a high χ-value but still give low dimer selectivities.

Ligand **L-10** ($P(OCH_2)_3CCH_3$, $\chi = 31$, $\Theta = 101°$) leads to a high cyclotrimer selectivity, as was reported previously.[8] The small size of the ligand easily allows the insertion of a third isoprene molecule, while the high χ-value ensures the formation of a cyclic product rather than a linear one.

Ligand **L-20** ($P(OCH_2CF_3)_3$, $\chi = 39.3$, $\Theta = 110°$) should in principle behave similarly. However, the rate is low and the product distribution is as follows: linear trimers 42%, cyclic trimer 23%, cyclic dimer 28%. Thus the trend is observed to some extend but the low rate suggests that inactive nickel species are formed (NiL_4?).

Ligand **L-18** ($P(OC_6H_4$-o-t-$Bu)_3$, $\chi = 29$, $\Theta = 175°$) must cause too much steric crowding in one of the complexes involved in the catalytic cycle. The conversion per hour of this catalyst is several times lower than the conversion with the *o*-Me analogue (14) and some 40% of higher oligomers is formed.

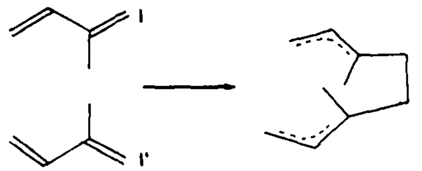
Ligands **L-5** and **L-6** ($P(OMe)_3$, $\chi = 23$, $\Theta = 107°$, and $P(O$-n-$Bu)_3$, $\chi = 20$, $\Theta 109°$) give rise to product distributions (linear trimers 10.25%, cyclotrimers 20%, cyclodimers 22 and 31%, respectively) with relatively large amounts of trimers, which is indicative of a facile insertion of a third isoprene molecule and a slow elimination of the organic moiety from the Ni complex intermediate.

As stated before, there is one exception, viz. $P\phi_2(O\phi)$, which although having the right cone angle (139°) fails to give a high cyclodimer selectivity. It reacts as if it belonged to the more basic group of ligands ($\chi < 15$), which all lead to low dimer contents and large amounts of linear oligomers.

DISCUSSION OF THE MECHANISM

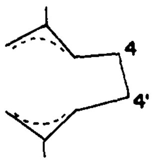
(a) *The formation of the metallacycle.* In this section we will concentrate on the ligand systems that yield mainly cyclodimers, i.e. ligands with χ-values > 20 and

$125° < \theta < 152°$, and discuss the regioselectivity changes found. In the first step of the reaction a bis-allylic Ni complex is formed by coupling two isoprene molecules. Initial C–C bond formation may take place between two



7

C-1 atoms of isoprene, leading to head-to-head dimers*(7), or between two C-4 atoms giving tail-to-tail products (8), or a C-1 to a C-4 coupling, giving head-to-tail dimers (9):



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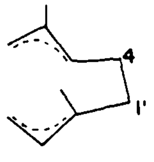

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The bis(allyl)Ni complex can have the two allyl groups π-bonded, or σ-bonded to either end, or there may be a combination of these bonds. In the present discussion we will pay no attention to precise structure of the relevant intermediates and confine ourselves to the electronic influences of the addition and elimination processes using schematized structures.

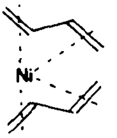
The determination of the initial coupling mode (head-to-tail selectivities) can take place in two manners: (a) step (1) of the reaction is rate determining and then the mode is established here, or (b) step (2) of the reaction sequence is slower than the reverse reaction ($k_{-1} > k_2$) and then the selectivity to head-to-tail coupling modes is determined by the product of the concentration of the particular isomer of 7–9 in the established pre-equilibrium and the k_2 for that particular isomer:

$$\mathrm{Ni(diene)_2} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Ni(allyl)_2} \qquad (1)$$

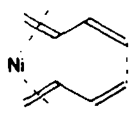
$$\mathrm{Ni(allyl)_2} \xrightarrow{k_2} \text{products} \qquad (2)$$

For ligands with high χ- values the former situation is more likely, due to promotion of the reductive elimination.

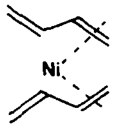
The cyclometallation step can occur in several ways in close or less close proximity to the Ni atom:



10a

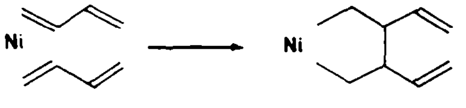


10b



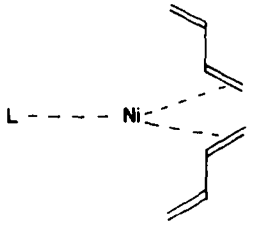
10c

Asymmetric combination of structures 10a, b and c can also be visualized. The difference between a and c is a matter of mono- or bidentate coordination of the dienes. In case b the cyclization reaction is a [4+4+2] instead of a [2+2+2] reaction. In the following, structure c will be used, which seems justified considering the structure of the starting material and the fact several cyclometallations are known as a six-electron process with mono-olefins.[19–23] Conjugation does play a role where it changes the levels of the orbitals, making dienes more reactive. In effect, π-allyl formation contributes to the way of cyclometallation as addition (3) has not been observed.



(3)

The structure of the starting olefin complex is presumably trigonal with the C–C bonds of the coordinating half of the diene lying in the coordination plane one position being occupied by a third ligand:



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as was found[24] for (tricyclohexylphosphine)(bis-ethylene)nickel(0) and as has been predicted for this type of complex.[25] The cyclometallation reaction has been described as a hetero-ring-closure reaction occurring in the sense of the Woodward-Hoffmann rules, with each step being symmetry controlled.[26] However, this approach with the symmetry rules only does not enable predictions to be made concerning the regioselectivity. A preliminary note outlining steps towards the use of frontier orbitals[12] on this type of reactions was published by Pearson.[27]

In Fig. 4 we have drawn the orbitals involved in the

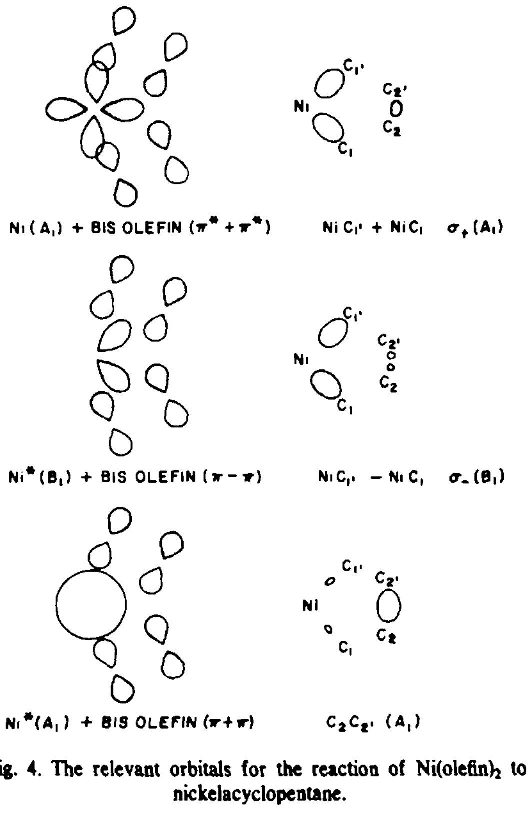


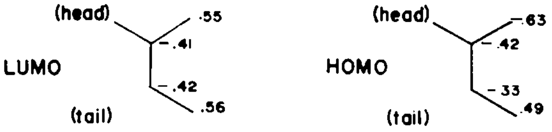
Fig. 4. The relevant orbitals for the reaction of $\mathrm{Ni(olefin)_2}$ to nickelacyclopentane.

cyclometallation. The one at the top shows the interacting filled Ni 3d-orbital with one of the combinations of the anti-bonding olefin orbitals ($\pi^* + \pi^*$) which eventually leads to the symmetric combination of the two Ni–C bonds. The two lower ones show the interaction of the filled olefin orbitals with Ni orbitals of corresponding symmetry. They do of course also interact with the filled Ni orbitals pushing them upwards, thus enhancing the back-donation as outlined by Rösch and Hoffmann.[25] The form of the orbitals drawn is rather arbitrary since extensive mixing will occur in this low symmetry. We have assumed C_{2v} symmetry and the orbitals to be formed in the metallacycle will have A_1 and B_1 symmetry (the Ni–C bonds) and A_1 symmetry (C_2–C_3 bond) originating from A_1 and B_1 electron pairs from the olefins and hence the Ni donates an A_1 pair. The remaining ligand(s) on the nickel will be regarded only as giving an overall raising or lowering of the Ni levels.

In Fig. 5 a simple qualitative interaction diagram is given for Ni-bis-olefin and nickelacyclopentane. It is seen how the three orbitals given in Fig. 4 correlate in the two molecular structures. The B_2 and A_2 orbitals correlate with themselves and need not concern us here. It is seen, however, that formally the Ni complex would end up in a doubly excited state if the symmetry were to be preserved, and formally the reaction† is "forbidden". The role of the metal[29] is also to provide low-lying excited states that facilitate processes which otherwise would be extremely slow.

From the pictures in Fig. 4 immediately some conclusions with respect to the regioselectivity can be drawn. Formation of σ_+ (A_1) requires the highest coefficients in the olefin anti-bonding on C_1 and C_1'. Formation of C_2–C_2' requires maximum coefficients of the HOMO's on these positions although this counteracts the B_1 interaction. If we assume that the donation from Ni (A_1) into the symmetric antibonding combination is the critical interaction this also determines the regioselectivity. Applied to propane dimerization via cyclometallation on nickel this mechanism would lead to a linear dimer product.[30] Formation of asymmetric dimers from methylenecyclopropane cannot be explained with this simple approach.[32]

For conjugated dienes, regarded as mono-enes with the vinyl groups attached to C_1 and C_1' so as to allow resonance stabilization both HOMO and LUMO coefficients are higher at C_2' and C_2. Isoprene has the following coefficients[31]:



Again following a scheme whereby donation from Ni to isoprene is decisive it is seen that there will be very little preference, if any, in the region (head or tail) to be attacked by the Ni donor and hence we would expect a statistical distribution, as is indeed observed (see Results) for complexes with ligands having lower χ-values (Fig. 3). When the nickel levels are lowered (i.e. ligands with higher χ-values) the situation changes. It is suggested that in complexes with ligands of higher χ-values the filled orbital of isoprene become stereo-directing since Ni‡ orbitals are now closer. This leads to a preference of the head of the isoprene molecule to take part in the cyclometallation. This then results in the observed head-to-head coupling mode becoming predominant with Ni complexes that are relatively electron-deficient (Fig. 3).

(b) *The reductive elimination of the product*‡. Before turning to the elimination of terpene-type products from the isoprene-derived intermediates we will briefly discuss some experimental and theoretical features of simpler nickelacyclopentanes. From Fig. 5 one can easily derive the orbital correlation scheme shown in Fig. 6, which

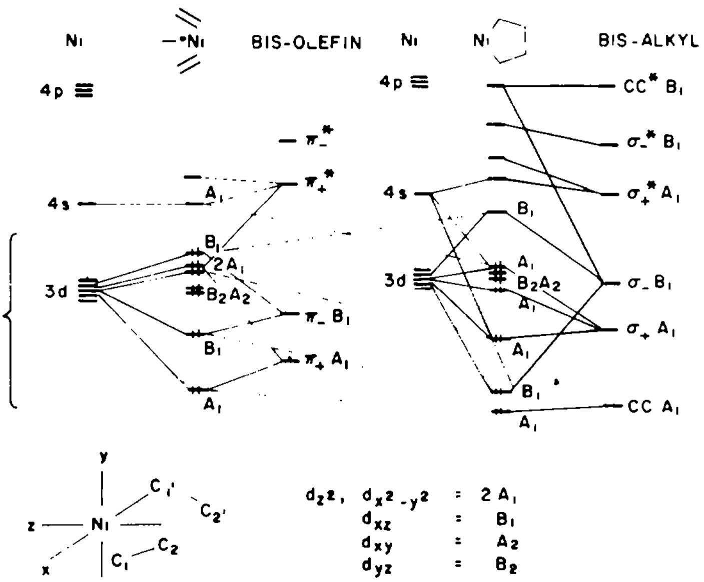


Fig. 5. Qualitative orbital schemes and correlation diagram (----) for the reaction of Ni(olefin)$_2$ to nickelacyclopentane.

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†The reaction differs in this respect from a carbene or SO_2 addition to a diene which is formally allowed.[28]

‡After completion of this manuscript a short communication was published presenting a similar treatment of the decomposition of metallacyclopentanes.[33] In this paper Braterman arrives at essentially the same explanation as the one given here as an introduction to the isoprene dimerization.

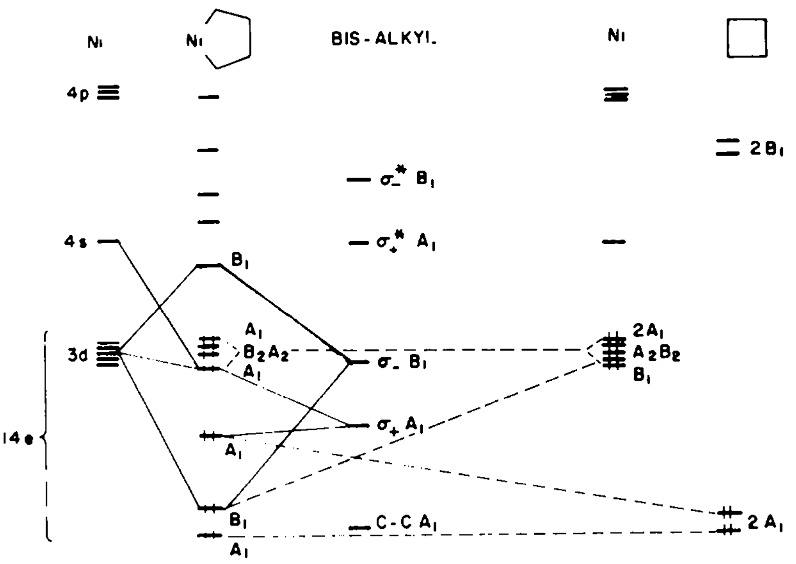
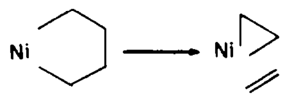
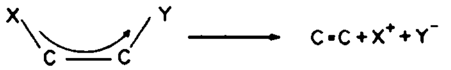


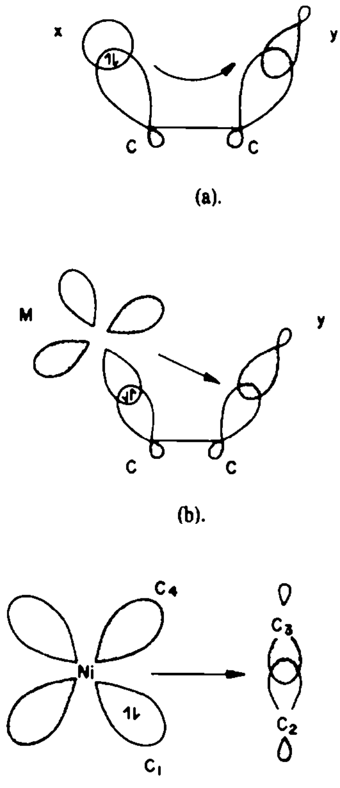
Fig. 6. Qualitative orbital schemes and correlation diagram(----) for the reaction of nickelacyclopentane to nickel (cyclobutane).

represents the reductive elimination of cyclobutane from nickelapentane. It follows that formally the reductive elimination with cyclobutane formation is the allowed process. The overall net process, the supra-supra-facial addition of two ethylene molecules, is forbidden but as outlined above, the first step of cyclometallation is a "forbidden" step interchanging an occupied B_1 and A_1 level. Formally one might say that, as is shown in Fig. 6, the asymmetric electron pair of the Ni–C bonds flows to the metal whereas the symmetric pair closes the butane ring. The asymmetric pair of Ni–C electrons (σ-, B_1) undergoes the strongest mixing with the metal orbitals of the two electron pairs forming the Ni–C bonds and this is therefore also the one that is most strongly influenced by the variation of the level of the metal orbitals. Strong donors on Ni (low χ-values of the ligand(s)) will raise the Ni levels and decrease the Ni component in the B_1 orbital, while strong acceptors will lower the Ni levels and concentrate the B_1 orbital on Ni. Hence ligands with high χ-values will stimulate reductive elimination giving cyclobutanes. Raising the Ni levels may result in bis-olefin formation, i.e. reversal of the first (formally forbidden) step. We will look at this reaction now from a slightly different angle and regard it as a special case of β-elimination:



As described by Klopman,[34] the process of X^+Y^- β-elimination can be visualized as a donation of the electron pair of the C–X bond into the accepting antibonding C–Y bond:





(a).

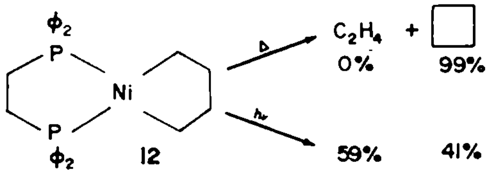
(b).

(c).

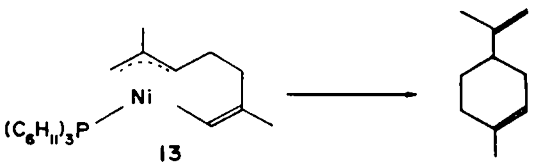
Fig. 7. The interacting HOMO and LUMO for three types of β-elimination.

With this mechanism the reaction becomes easier when the transfer of the electron pair is facilitated by an overlap of the donor pair and the acceptor orbital (Fig. 7a). In this case it is obvious that there is no concerted formation of an XY bond with the release of olefin. If X is replaced by a metal ion with d-orbitals (Fig. 7b) the β-elimination could be a concerted process when occuring in *cis*-fashion. This picture is somewhat simplified because other filled d-orbitals may contribute as well. Besides, a mechanism whereby the C–X→X^+ acts purely as a donor is too extreme when X is a transition metal and Y is a hydride since a reverse donor-acceptor interaction may also play a role here. What will happen in the present case is a donation of the occupied B_1 orbital (forming the Ni–C bonds, Fig. 7c, Fig. 4: σ-, B_1) to the anti-bonding C_2–C_2' orbital acting as the acceptor. This interaction will be the stronger the higher nickel orbitals are notwithstanding the fact that as a whole the reaction remains "forbidden". A third reaction that may take place on the metallacycle is β-hydrogen elimination, though this reaction is rather slow compared to that with n-alkyl complexes which was ascribed[35] to the steric inability of the metallacycle to allow of a co-planar MCCH configuration (Fig. 7b) optimal for cis-hydride elimination. Though sterically unfavourable in the metallacycle, this reaction will occur when the filled metal orbitals have been pushed upwards (strong donor ligands, low χ-values) and when in addition an open coordination site is available for the hydride ion.

The above orbital picture of the decomposition of the metallacycle finds ample experimental support from a variety of metal complexes. Several authors have already noted that oxidizing the metal, or complexing the complex with an electron-with-drawing ligand, enhances the formation of cyclobutanes. Addition of oxidizing agents or electron-with-drawing olefins increases the selectivity to cyclobutane.[36] Several reactions of this type have been reported[32,20,37] for nickelacyclopentane compounds. Non-cyclic examples are also known, e.g. dialkyl(dipyridine)nickel decomposes giving alkanes and alkenes;[38] however, in the presence of acrylonitrile the diethyl analogue produces butane,[39] which was explained by the increased electronegativity of nickel facilitating cleavage of the Ni–C bond. The occurrence of the "forbidden" reactions is prompted by electron-rich metal centres and, for example production of ethylene[35] from titanacyclopentane where the metal has a low electronegativity should not be surprising. In the light of considerations regarding the allowed or forbidden nature of the reactions, the results obtained with photodecomposition are very intriguing. Compound 12 was found to give upon thermal decomposition cyclobutane as the only[36b] product whereas photolysis yielded mainly ethylene. A second example[40] is provided by photolysis of a platinacyclopentane complex yielding ethylene upon irradiation.



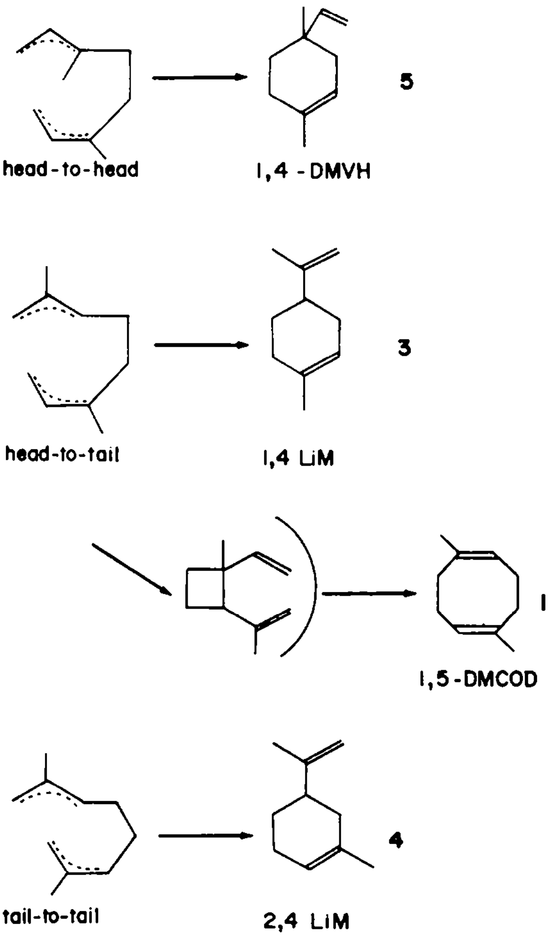
Isoprene-derived metallacycles show the same thermal reaction as the above-mentioned nickelacyclopentanes under the influence of electron-withdrawing additives; treatment of 13 with CO gave reduction elimination to limonene[18]



On the other hand, reaction of 13 with triphenylphosphine[18] yielded isoprene, demonstrating the effect of electron donors; the nickel orbitals are raised and the process depicted in Fig. 7c takes place.

The present results also show that with increasing χ-values the tendency to reductive elimination of cyclodimers and cyclotrimers increases, whereas the tendency to β-hydride elimination reactions leading to linear products decreases. The selectivity to cyclodimer versus cyclotrimer is determined by the ease of insertion of a third isoprene molecule versus elimination of the dimer, which is governed by the cone angle of the ligand: small cone angles and high χ-values gives cyclotrimers.

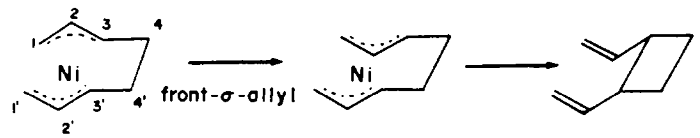
Figure 3 depicts the change in coupling mode of the two isoprene units vs the χ-value. However, it also expresses a change in the way the reductive elimination proceeds: although more of the head-to-head intermediate (precursor to 1,6-DMCOD) is formed at higher χ-values the amount of 1,6-DMCOD strongly decreases with increasing χ-values, thus giving a (head-to-tail) 1,5-DMCOD, which is even purer than at intermediate χ-values when there is less head-to-head coupling. With increasing χ-values there is an increasing tendency of the intermediates to decompose to one particular product. These reactions can be summarized as follows, irrespective of whether the allyl groups are in the π- or σ-form or whether they have the *cis*- or *trans*-conformation (Scheme 1). The head-to-tail intermediate gives two products with the 8-membered ring predominating. The cyclobutane derivative might be an intermediate which rearranges via a Ni-catalysed Cope reaction to the cyclooctadiene derivative.[41] The overall picture that emerges is that at higher χ-values the symmetric inter-



Scheme 1.

mediates (head-to-head, and tail-to-tail) show an increasing tendency to give an "asymmetric" product, viz. a 6-membered ring, whereas the asymmetric intermediate shows a preference for a "symmetric" coupling.

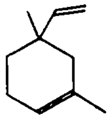
The formation of a 6-membered ring requires one double bond (or allyl group) to be in the *cis*-form, while the formation of an 8-membered ring requires two *cis*-configurations unless it takes place via Cope rearrangement of a cyclobutane, for which there are no such requirements in this respect. According to Stephenson's findings[14] (for butadiene) the first intermediate formed has an *anti*-bis-allyl structure, which rearranges to the *syn*-bis-allyl structure before reductive elimination to *cis*-divinylcyclobutane occurs via "front-σ-allyl forms" with preservation of the *trans*-configuration of the double bonds:



(front-σ-allyls are C_1-σ-allyl groups)

If the only effect of higher χ-values would be an acceleration of the reductive elimination one might expect even more cyclobutane or cyclooctadiene-based compounds since other products require a π-σ rearrangement at the C_3 or C_3' atom to form a *cis*-allyl. Since this is not expected that ligands with high χ-values promote π-σ rearrangements[42,43] the initial compound could be formed from cisoid isoprene molecules.

For a description of the elimination two extreme approaches seem possible: an orbital—and a charge-controlled mechanism, of which the former definitely requires structural suppositions. An oversimplified ionic mechanism would involve the ring closure of the octadienyl fragment containing an allyl cation and an allyl anion which in the case of head-to-head and tail-to-tail intermediates would clearly result in cyclohexene formation provided that at least one *cis*-allyl is present. The head-to-tail intermediate should result in 2,4-DMVCH (**14**), a product not found at all.



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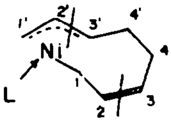
This invalidates a purely ionic description.

The assumption that the intermediate isolated in similar systems[18] is also formed in the present catalytic system, in combination with the orbital picture given above for reductive elimination at a nickelacyclopentane, leads to straightforward formation of the cyclohexene derivatives of all three (or four, *vide infra*) intermediates. Though intermediate **13** has no symmetry element the bonding scheme will be comparable to that of cases having C_{2v} symmetry, and the situation will be similar to that with the nickelacyclopentane where cyclobutane is provided when the B_1 orbital is mainly concentrated on the metal in that now a C–C bond will be formed between C_3' and C_1 as the allowed reaction. This is the reaction to be expected with ligands with the high χ-values.



13

As indicated above, four isomers for intermediate **13** may be expected (head-to-head, tail-to-tail, head-to-tail, tail-to-head). Of the two isomers envisaged for the head-to-tail isomer the 2′,3-Me$_2$-isomer will be more stable on account of hyperconjugation effects than the 3′,2-Me-one, which explains the absence of 2,4-DMVCH (**14**), the formation of which becomes sterically highly unfavorable.

In our opinion, the increasing rate observed with the simultaneous increase of the selectivity in the reductive elimination in the sense described above when going to nickel complexes with ligands with increasing χ-values clearly point to an orbital-controlled reaction although this is less clear in the elimination step than in the oxidative addition step.

EXPERIMENTAL

(c) *Isoprene dimerizations.* The experiments were performed in a 100-ml stainless-steel (AISI-316) autoclave. The autoclave was stirred magnetically and filled under argon/nitrogen.

The standard experiment was carried our as follows: The stirred autoclave was placed in an ice bath and charged with 1.5 mmol of the phosphine/phosphite, 0.2 mmol of N-Me-pyrrolidone and a solution of 0.5 mmol of Ni(acac)$_2$ in 4 ml of THF. Then 50 ml of isoprene was introduced. Finally a solution of 3.0 mmol triethylaluminium in 10 ml of isooctane was slowly added. After closing, the autoclave was heated for the required period, cooled down, opened and the reaction mixture analysed.

Materials. The Ni(acac)$_2$, N-Me-pyrrolidone, triethylaluminium, phosphines/phosphites not mentioned in the preparations and the isoprene were obtained commercially. Ni (acac)$_2$ was dried overnight at 85°/0.5 mmHg; the solvents and the isoprene were dried and distilled prior to use.

Glc analysis. The glc analysis were carried out on a H&P 5750 instrument. Yields of the dimers, trimers, etc. were calculated after analysing the reaction mixture on a 10% SE-30/chromosorb W dimethyldichlorosilane acid-washed 80–100 mesh 3.6 m × 3 mm column, using isooctane as an internal standard. The various isomers of the dimers were analysed on a capillary column, 50 m × 0.25 mm with poly-*m*-phenyl ether 7-ring as the liquid phase.

^{13}C NMR data of products (in $CDCl_3$, δ from TMS). The products were identified by comparison with authentic samples (1,5-DMCOD, 1,4-LIM) or by their their ^{13}C NMR spectra and off-resonance decoupling.

(**1**) 1,5-DMCOD; 135.6, 33.7, 26.3, 122.8, 26.5

(**2**) 1,6-DMCOD; 135.6, 32.5, 26.3, 122.8, 27.8

(**3**) 1,4-LIM; 149.9, 133.5, 120.9, 108.7, 41.3, 31.1, 30.8, 28.2, 23.5, 20.8

(**4**) 2,4-LIM; 149.7, 133.4, 120.9, 108.7, 41.9, 35.8, 27.6, 25.9, 23.7, 20.8

(**5**) 1,4-DMVCH; 147.7, 132.7, 119.6, 110.3, 36.9, 34.6, 34.1, 27.8, 25.7, 23.3

(**6**) DMVCB; 145.5, 142.5, 111.1, 109.3, 52.4, 45.4, 30.6, 27.1, 22.0, 19.6.

Preparation of the phosphites (for formulae and ligand number see Table 1)

Method A. A soln of 0.1 mol PCl_3 in 50 mm dry ether was added in 1 hr to a stirred soln of 0.3 mol alcohol and 0.3 mol pyridine in 250 ml dry ether at −10°. Subsequently the mixture was warmed and refluxed for 1 hr. After cooling down the formed pyridine HCl salt formed was filtered off and washed twice with 50 ml portions ether. From the combined washings and filtrate the ether was distilled off and the residue distilled *in vacuo*. All manipulations were done under atmosphere of Ar or N_2.

Method B. An amount of 0.1 mol of PCl_3 was added at ambient temp to a soln of 0.3 mol phenol and 0.01 mol dimethylaniline in 100 ml xylenes. The mixture was slowly heated to reflux, while N_2 was passed through to expel the HCl formed. After refluxing for 2 hr, the xylenes were distilled off and the residue was kept at 180° overnight. Recrystallization or distillation of the residue yielded the phosphites.

The mixed phosphite $P(O\phi)_2(Oi\text{-}C_3HF_6)$ was prepared by refluxing $P(O\phi)_3$ with one equivalent of hexafluoroisopropanol for 4 hr followed by distillation (bp. 95°/0.1 mm; yield ~ 10%). (^1H NMR, δ: 5.30 m(1 H), 7.20(10 H), $J_{PH} = 10$ Hz $J_{FH} = 6$ Hz). The mixed phosphite $(PO\phi)(Oi\text{-}C_3F_6H)_2$ was prepared by reacting $P(O\phi)Cl_2$ with two equivalents of hexafluoroisopropanol according to method A (bp. 100°/20 mm Hg)(^1H NMR δ: 5.04(2 H), 7.25(5 H)).

Other ligands. Ligand L-11 was prepared from tetramethyl-1,2-ethanedioxyphosphorous chloride and t-BuOH via method A (bp. 98°/19 mm Hg, yield 90%) (^1H NMR, δ: 1.23(6 H), 1.38(6 H), 1.40(9 H) with $J_{PH} = 0.76$ Hz). Ligands L-28 and L-29 were prepared according to literature procedures.[44,45] Ligand L-31 was prepared from tetramethyl-1,2-ethanedioxyphosphorous chloride and an excess of morpholine in 60% yield (^1H NMR, δ: 1.23 broad s (12 H) 2.9(4 H) 3.7(4 H) nonresolved m) (bp. 88°/0.3 mm).

Acknowledgements—The authors are indebted to Dr. T. A. B. M. Bolsman for stimulating and valuable discussions.

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