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INFLUENCES OF OLEFINIC AND DIKETONATE LIGANDS IN THE NICKEL-CATALYZED LINEAR OLIGOMERIZATION OF 1-BUTENE

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Summary

Cyclooctenyl nickel complexes which contain cyclic 1,2-diketones, α-acyl cycloalkanones, or substituted 1,3-propanediones as chelating ligands have been shown to be active catalysts for the homogeneous linear oligomerization of 1-butene. An almost linear correlation between acidity and activity of the ligands was observed.

Three new η^1,η^2-cyclooctenyl diketonate complexes, containing dibenzoylmethane, furoylbenzoylmethane and di-(*para*-fluorobenzoyl)methane, respectively, as the chelating ligand were prepared, and shown to be active catalysts. Nickel diketonate complexes containing η^3-cyclooctenyl, η^3-allyl, and η^3-butenyl ligands confirmed that η^3-allyl species are less active than their η^1,η^2-analogues. This may be attributed to the ease of nickel hydride formation in η^1,η^2-olefin complexes.

Introduction

The linear oligomerization of olefins yields higher olefins which are desirable products in the industrial synthesis of detergents, surface active compounds, lubricating oils and plasticizers. However, use of the majority of transition metal catalysts gives branched oligomers, and only a few catalyst systems are known which lead to linear products [1]. Nickel complexes with chelate ligands such as phosphorus-oxygen [2] or arsine-oxygen [3] catalyze the linear oligomerization of ethene to exclusively linear α-olefins. We have reported that cyclooctenyl-nickel complexes with β-diketonate ligands are active oligomerization catalysts or catalyst precursors for olefins such as propene, butene, hexene and octene [4]. In our attempt to elucidate the function of the β-diketonate and cyclooctenyl ligand we have studied a variety of diketones. In addition the allylic part of the nickel complex has been varied and selected compounds have been isolated and their catalytic properties investigated.

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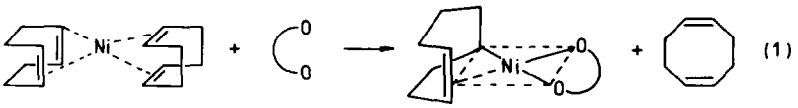
Results and discussion

Variation of the diketonate ligand

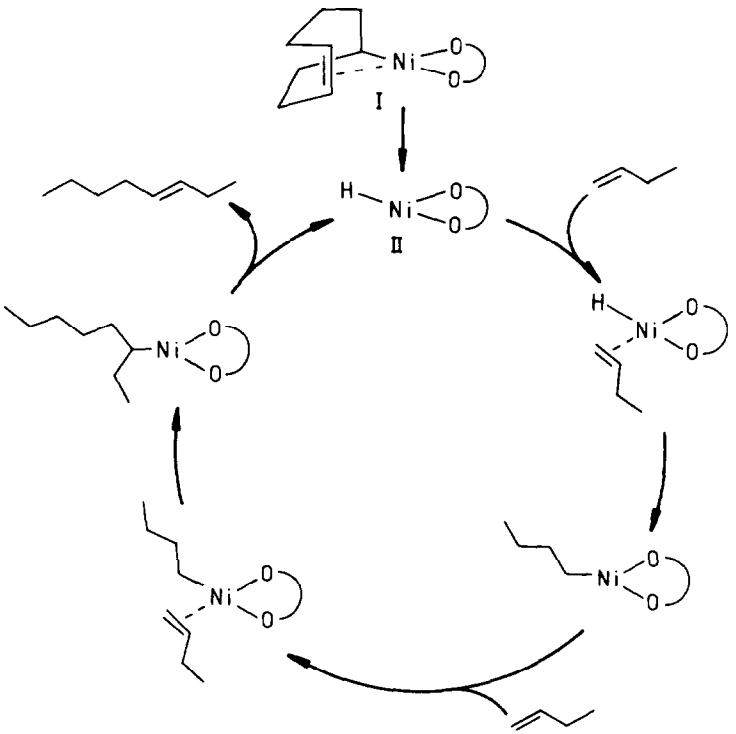
In order to investigate the influence of the diketonate ligand complexes were prepared in situ by the method illustrated in eq. 1 for the reaction of bis(1,5-



(1)

I

cyclooctadiene)nickel(0) [$Ni(cod)_2$] and a diketonate chelate ligand. The complex I formed is considered to be the catalyst precursor. As outlined in Scheme 1,



SCHEME 1

elimination of the C_8-moiety leads to a nickel hydride (compound II), which reacts with 1-butene to give 3-octene.

The proposed hydride mechanism has been supported by isolation of the nickel hydride complex $[(P(C_6H_{11})_3]_2(CF_3COCHCOCF_3)NiH$, in which the hydride is stabilized by two molecules of tricyclohexylphosphine [5]. Further evidence for a hydridic intermediate in a catalytic system is obtained by addition of triphenylphosphine to complex I. The ^1H NMR nickel hydride resonance is found at -16 ppm [6].

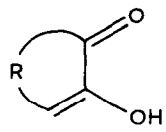
A series of 1,2- and 1,3-diketones were treated in situ with a molar equivalent $[Ni(cod)_2]$ according to 1. 1-Butene was then added to the solution, which was

stirred in a glas autoclave for 1 h at 70°C. The products consisted of butene oligomers in a Schulz-Flory distribution. The C_8-dimers and C_{12}-trimers amount to > 90%.

Cyclic 1,2-diketones

R = $(CH_2)_n$ n = 2,3,4

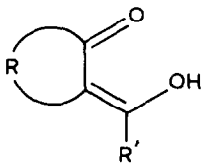
tropolone



α-Acyl-cycloalkanones

R = $(CH_2)_n$ n = 3,4,5

R' = CH_3 , H

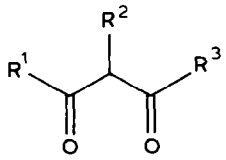


1,3-Disubstituted 1,3-propanediones

R^1 = CH_3 , Ph , 2-Furyl , CF_3

R^2 = H , CH_3 , F

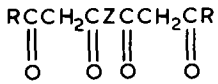
R^3 = CH_3 , Ph , 2-Furyl , CF_3



Linear bridged bis-β-diketones

Z = C_2H_4 , C_4H_8 , C_8H_{16} , C_6H_4

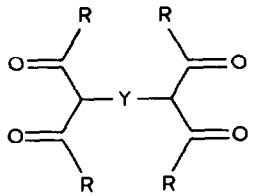
R = CH_3 , Ph



Central bridged bis-β-diketones

Y = CH_2 , C_2H_4 , CHPh , C_4H_8 , $C_{10}H_{20}$

R = CH_3 , Ph



SCHEME 2

Scheme 2 lists the various groups of diketones studied. About 44 different ligands were tested [7]. A remarkable dependency of the activity of the catalyst on acidity of the ligand was observed, as illustrated in Fig. 1 and Table 1. It seems that the acidity of the ligand is dominating for the catalytic activity, the activity increasing almost linearly with increasing acidity. The best ligand is hexafluoroacetylacetone with a pK_a of 4.2, followed by trifluoroacetylacetone ($pK_a = 4.7$). It can be expected that ligands with higher acidity will be even more active, but we have not been able to confirm this because of the non-availability of compounds soluble in nonpolar organic solvents.

The driving force for formation of complexes of type I, in which one hydrogen of the diketone is transferred to one 1,5-cyclooctadiene ring of bis(1,5-cyclooctadiene)nickel(0) (eq. 1), seems to originate in the acidic nature of the enol form, leading to stabilization of a 6-membered chelate ring.

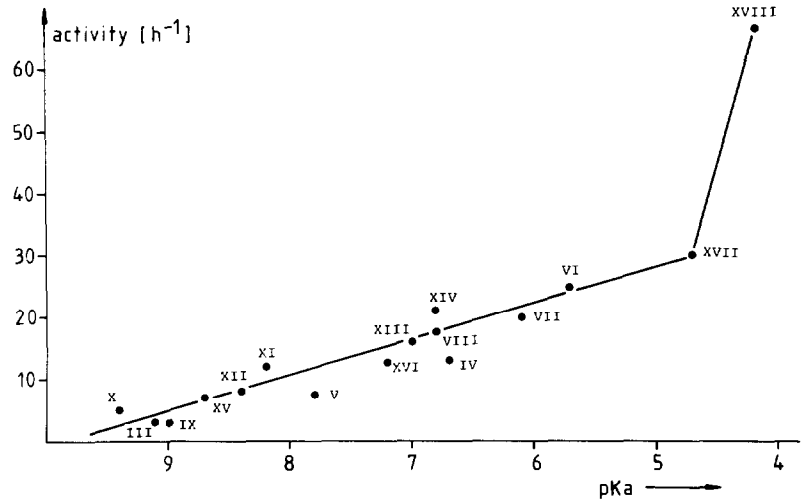


Fig. 1. The dependency of the activity of the catalyst on acidity of the ligand.

TABLE 1

OLIGOMERIZATION OF 1-BUTENE WITH IN SITU CATALYSTS

Ligands			Enol-form (%)	pK_a	Activity (mol products)/(mol Ni h)	Oligomers		Linearity	
						C_8 (%)	C_{12}	C_8 (%)	C_{12}
Cyclic 1,2-diketones	R								
III	$(CH_2)_2$		91	9.1	3	88	12	50	–
IV	tropolone		100	6.7	13	75	25	58	–
α-Acyl-cycloalkanones	R	R′							
V	$(CH_2)_3$	CH_3	83	7.8	7	89	11	77	–
VI	$(CH_2)_3$	H	89	5.7	25	90	10	84	65
VII	$(CH_2)_4$	H	99	6.1	20	86	14	82	66
VIII	$(CH_2)_5$	H	99	6.8	18	83	17	79	62
1,3-Disubstituted 1,3-propanediones[a]	R^1	R^3							
IX	Me	Me		9.0	3	90	10	86	–
X	Me	Ph		9.4	5	85	15	86	55
XI	Ph	Ph		8.2	12	87	12	84	60
XII	Ph	Fu		8.4	8	83	16	82	55
XIII	Ph	FPh		7.0	16	80	20	80	59
XIV	Ph	CF_3		6.8	21	87	12	81	58
XV	Fu	Fu		8.7	7	88	12	81	–
XVI	Fu	CF_3		7.2	13	80	19	81	56
XVII	Me	CF_3		4.7	30	89	10	79	57
XVIII	CF_3	CF_3		4.2	66	87	11	77	56

[a] Abbreviations: Me = Methyl; Ph = Phenyl; FPh = 4-Fluoro-phenyl; Fu = 2-Furyl; R^2 = H.

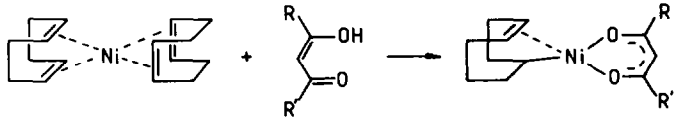
A high degree of enolisation, implying a tendency to form the cisoid conformation preferentially, and a related high acidity appears to be the most important requisites for suitable diketone ligands.

Substitutions were also carried out in position R^2 of the 1,3-propanedione. Neither electron donating groups nor electron withdrawing groups showed a significant effect. The linear bridged bis-β-diketones and central bridged β-diketones gave moderately active catalysts [7].

Variations of the olefinic allyl group

To investigate the influence of the olefinic C_8-allylgroup in I, various complexes of type I were isolated. The use of well-characterized compounds as catalysts or precursors for catalysts has many advantages, since in situ methods never allow determination of the extent of complex formation. Spectroscopic monotoring of the catalysed reaction is often precluded by the presence of many species.

η^1,η^2-Cyclooctenyl complexes. Use of the reaction shown in eq. 2 permitted



(2)

	XIX	XX	XXI	XXII	XXIII	XXIV
R	Me	Me	CF_3	Ph	Ph	4FPh**
R'	Me	CF_3	CF_3	Ph	Fu*	4FPh**

* Fu = furyl

** 4FPh = p-fluoro-phenyl

isolation of the nickel η^1,η^2-cyclooctenyl complexes XIX–XXIV. The spectroscopical data for the complexes XIX–XXI have already been published [4]. The structure of the new complexes XXII–XXIV was confirmed by their ^{1}H NMR data, shown in Table 3. The η^1,η^2-cyclooctenyl ligand is identified by the two protons H_a and H_b which are strongly shifted to the high field and by the two olefinic protons H_e and H_f in the region of 5.05 to 5.75 ppm.

TABLE 2

COMPARISON OF ISOLATED AND IN SITU CATALYSTS

Catalyst	Activity (mol products)/ (mol Ni h)	Oligomers (%)			Linearity (%)		
		C_8	C_{12}	C_{16}	C_8	C_{12}	C_{16}
XXII isolated [a]	119	75	21	4	76	56	43
XXII in situ [b]	12	87	12	–	84	60	–
XXIII isolated	79	80	19	1	81	56	43
XXIII in situ	8	83	16	–	82	55	–
XXIV isolated	85	72	23	5	80	–	–
XXIV in situ	18	80	19	–	80	59	–

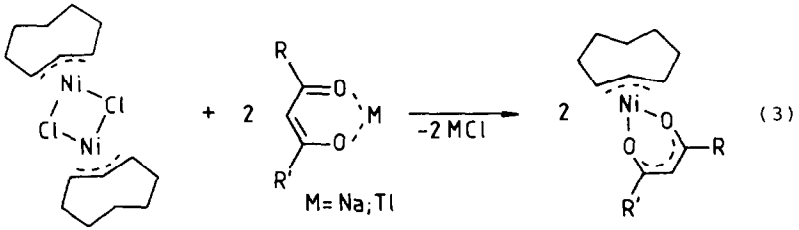
[a] t 1 h, c 0.025 mmol/l, T 90°C. [b] t 1 h, c 0.020 mmol/l, T 70°C.

The IR data (Table 4) confirm the coordination of the β-diketone to the nickel, revealed by the high shift from the region of 1600–1650 cm^{-1} typical for the free ligands to 1510–1515 cm^{-1} for the bonded diketone. The signal of the nickel–oxygen bond is found between 680 and 700 cm^{-1}. The double bond of the cyclooctenyl entity shows up in signals at 1595 cm^{-1} and 3010–3100 cm^{-1}.

Mass spectra confirm the composition via the molecular peaks M^+ in the ratio of the isotopes of ^{58}Ni and ^{60}Ni of about 2.6/1 and the other expected fragments are also observed (Table 5).

The catalytic activities of complexes XXII–XXIV in the oligomerization of 1-butene were investigated. Table 2 lists results which allow comparison of the in situ systems with those for catalysis by the isolated nickel complexes. In general, the isolated complexes are about 10 times more reactive. After optimization of the reaction conditions values of 1200 mol products/mol Ni h were achieved for 1-butene [4,5]. The selectivities of the various catalyst systems proved to be very similar. In all cases the dimers are formed with a linearity of about 80% and the trimers with about 55%. Use of the isolated complexes also leads to formation of tetramers, the hexadecenes, and in this case the linearity amounted to about 40%.

η^3-Cyclooctenyl complexes. According to eq. 3 the η^3-cyclooctenyl diketonate complexes XXV–XXVIII could be synthesized. Complex XXV has previously been prepared by Nüssel [19].



(3)

	XXV	XXVI	XXVII	XXVIII
R	Me	Me	CF_3	Ph
R'	Me	CF_3	CF_3	Ph

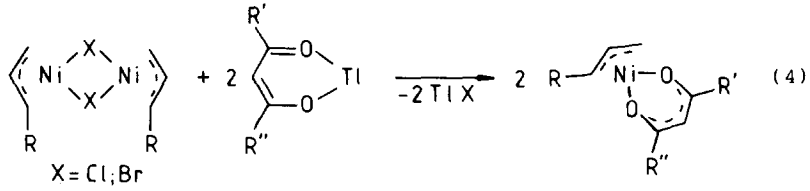
The ^1H NMR data (Table 6) confirm the η^3-character of the cyclooctenyl ligand. In all cases the *meso*-proton H_d appears as a triplet in the region of 5.25–6.00 ppm. The two c protons show a quartet in the range 3.35 to 4.10 ppm and the coupling constant $J_{c,d}$ is about 8 Hz. The influences of the various substitutents in the diketones on the chemical shifts of the cyclooctenyl protons can also be seen in Table 6.

The MS data confirm the composition of the complexes XXV–XXVIII (Table 7). The molecular peaks M^+ have the expected $^{58}Ni/^{60}Ni$ isotope ratio. In the spectra of XXVI and XXVII the fragment $m/e = 67$ which derives from the cyclooctadienyl ligand forms the base peak.

Surprisingly, the complexes XXV–XXVIII are practically inactive for oligomerization of 1-butene. This is remarkable since these complexes are the allylic isomers of the active complexes XIX–XXII. This observation must be related to the olefinic substituent, and more specifically must reflect the nature of the bonding of η^3-cyclooctenyl or η^1,η^2-cyclooctenyl as ligand. To explain this surprising finding we suggest that elimination of cyclooctadiene to form a nickel hydride complex II is

much more easier from the η^1,η^2-cyclooctenyl than from the η^3-cyclooctenyl ligand. It thus seemed of interest to study other η^3-allylic complexes involving the diketonate ligands found to be most active in the 1-butene oligomerization.

η^3-Allyl and butenyl complexes. The new η^3-allyl and butenyl complexes XXIX–XXXII were prepared according to eq. 4. Their [1] NMR data are listed in



(4)

	XXIX	XXX	XXXI	XXXII
R	H	H	Me	Me
R′	CF_3	Ph	CF_3	Ph
R″	CF_3	Ph	CF_3	Ph

Table 8. The allyl complexes show the singlet of the diketonate proton H_e, the septet of the allylic *meso*-proton H_a, the doublet of the *syn*-protons H_b ($J_{a,b}$ 7.2 Hz) and the doublet of the *anti*-protons H_c ($J_{a,c}$ 13.5 Hz). The crotyl complexes give a signal of the additional methyl group at about 0.5 ppm.

The IR spectra are shown in Table 9. The expected bonds were observed; for example that of the nickel–oxygen bond at about 680 cm^{-1} and that of the symmetrical deformation peak of the methyl group of the crotyl ligand at about 1375 cm^{-1}.

The MS data (Table 10) also confirm the proposed composition. All the spectra show the molecular peak M^+; in the case of complex XXIX this peak is present in unexpectedly high abundance. Typical fragments, for example of the ligands hexafluoroacetone (m/e = 98, 97, 69) and dibenzoylmethane (m/e = 224, 223, 147, 105) are also listed in Table 10.

The activity of the η^3-allyl and η^3-crotyl complexes XXIX and XXXI in the oligomerization of 1-butene is very low; the analogous complexes with dibenzoylmethane ligands (XXX and XXXII) are completely inactive.

Conclusions

The oligomerization of 1-butene was studied for 44 diketone and tetraketone ligands. The formation of predominantly linear dimers is favoured, reaching values of > 80%. The acidity of the diketones is the dominant influence on the properties of the catalyst, an almost linear correlation between pK_a and activity being observed. The best ligand is hexafluoroacetylacetone. Isolated complexes showed a much higher activity, than those generated in situ.

Surprisingly, η^3-allylic complexes, even those containing the most active ligand hexafluoroacetylacetone ligand, are practically inactive, and ease of nickel hydride formation may be responsible for this. Complexes containing the η^1,η^2-cyclooctenyl ligand can eliminate the C_8-ring much easier than those containing η^3-cyclooctenyl. It is remarkable that such fine differences in the olefinic part of the ligand have such large effects.

Experimental

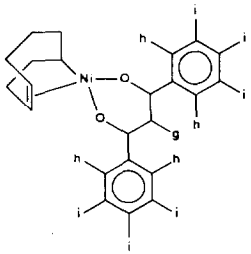
^{1}H NMR spectra were recorded on a Varian EM 390 instrument at 90 MHz and on a Bruker CXP 200 instrument at 200 MHz. Chemical shifts are reported as δ values relative to tetramethylsilane (TMS) as internal standard, except that for η^1,η^2-cyclooctenyl complexes benzene (δ 7.27 ppm) was used as the reference. Infrared spectra were recorded on a Perkin–Elmer 577 spectrometer using KBr cells or alkane solutions (Table 9). Mass spectra were obtained on a Varian MAT 112 S system. GLC analysis was carried out on a Carlo Erba 2300 AC instrument using a 50 m OV 101 capillary column (ID 0.25 mm) at 70 to 230°C (initially 6 min isothermal, then heating rate 8°C/min). A Spectra Physics SP 4000 instrument was used for peak integration.

The oligomerization with in situ catalysts was involved the following general procedure: 0.25 mmol $Ni(cod)_2$ was suspended in toluene and a toluene solution of 0.25 mmol ligand was added dropwise at −20°C. The 0.02 molar catalyst solution obtained was stirred for 15 min then transferred to a 40 ml glass autoclave. After addition of about 5 g 1-butene the solution was stirred at 70°C for 1 h. All reactions were carried out under argon.

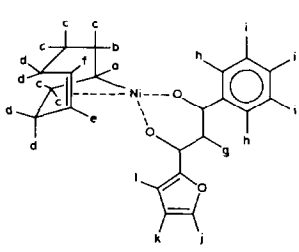
$Ni(cod)_2$ was prepared by the method of Wilke and Bogdanović [8]. 1-Butene, a commercial product, was dried over 4 Å molecular sieve. Acetylacetone (IX),

TABLE 3

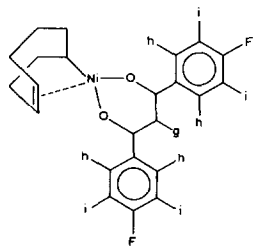
^{1}H NMR DATA OF THE NICKEL η^1,η^2-CYCLOOCTENYL COMPLEXES XXII–XXIV



XXII



XXIII



XXIV

Peak asignment	δ(ppm)	Integr.	δ(ppm)	Integr.	δ(ppm)	Integr.
H_a	−0.20–0.15 (m)	1	−0.25–0.10 (m)	1	−0.15–0.20 (m)	1
H_b	0.25–0.65 (m)	1	0.35–0.65 (m)	1	0.30–0.65 (m)	1
H_c	1.40–2.20 (m)	5	1.55–2.45 (m)	5	0.80–1.55 (m)	5
H_d	2.25–2.28 (m)	4	2.55–3.05 (m)	4	1.65–2.25 (m)	4
H_e	5.05–5.35 (m)	1	5.05–5.30 (m)	1	5.10–5.35 (m)	1
H_f	5.50–5.75 (m)	1	5.45–5.70 (m)	1	5.45–5.65 (m)	1
H_g	6.60 (s)	1	6.65 (s)	1	6.40 (s)	1
H_h	7.70–7.79 (m)	4	7.80–7.95 (m)	2	7.55–7.75 (m)	4
H_i	7.30–7.50 (m)	6	7.50–7.65 (m)	3	6.75–6.95 (m)	4
H_j	–		7.45 (d)	1	–	
H_k	–		6.40–6.55 (d)	1	–	
H_l	–		6.90–7.05 (d)	1	–	

TABLE 4

IR DATA OF THE NICKEL η^1,η^2-CYCLOOCTENYL COMPLEXES XXII–XXIV

Peak asignment	IR data (cm^{-1})		
	XXII	XXIII	XXIV
=C–H	3060–3030	3140–3020	3100–3010
–C–H	2950–2820	2980–2790	2970–2840
C=C	1593	1595	1598
C–O	1555–1505	1560–1510	1575–1515
C–C	1485–1440	1440–1370	1495–1370
C–F	–	–	–
Ni–O	681	698	693

hexafluoroacetylacetone (XVIII) and tropolone (IV) were commercial products. The literature methods used to prepare the other diketones are as follows: III [9,10], V [11], VI [12], VII [13], VIII [14], X [15], XI [16], XII [15], XIII [17], XIV [18], XV [15], XVI [18], XVII [18].

Complex isolation

All reactions were carried out under argon. Bis-η^3-cyclooctenyl-μ,μ'-dichlordinickel was prepared by the reaction of $Ni(cod)_2$ with 1-chloro-2-cyclooctene [20]. Complexes $[NiCl(C_3H_5)]_2$ and $[NiBr(C_4H_7)]_2$ were synthesized analogously from $Ni(cod)_2$ and allyl chloride or crotyl bromide [20]. The preparation of the thallium salts of the diketones was described by Hartmann [21] and Nelson [22].

Preparation of the η^1,η^2-cyclooctenyl nickel diketonate complexes XXII–XXIV

32 mmol $Ni(cod)_2$ were dissolved in 150 ml toluene at $-20°C$, and a solution of 32.5 mmol of the corresponding diketone in 50 ml toluene was added dropwise

TABLE 5

MS DATA OF THE NICKEL η^1,η^2-CYCLOOCTENYL COMPLEXES XXII–XXIV

XXII			XXIII			XXIV		
m/e	rel.Int. (%)	Ion	*m/e*	rel.Int. (%)	Ion	*m/e*	rel.Int. (%)	Ion
390/392 [e]	(3.1/1.3)	M^+	380/382 [e]	(4.9/1.8)	M^+	426/428 [e]	(5.4/2)	M^+
280/282 [e]	(23/9)	$M^+ - cod$	272/274 [e]	(28.6/8.2)	$M^+ - cod$	318/320 [e]	(11.2/4.5)	$M^+ - cod$
224	(6)	L [a]	214	(16.7)	L [b]	260	(8)	L [c]
223	(7)	L-H	147	(3.2)	L-furyl	259	(12.5)	L-H
147	(6)	L-Ph	137	(8.4)	L-Ph	165	(17.5)	L-FPh [d]
109	(12.5)	C_8H_{13}	110	(3.9)	C_8H_{14}	123	(100)	FPhCO
108	(14)	cod	108	(15.1)	cod	108	(1.8)	cod
105	(28)	PhCO	105	(100)	PhCO	95	(57.6)	FPh
77	(36)	Ph	95	(26.6)	furoyl	69	(8.6)	C_3HO_2
69	(14)	C_3HO_2	77	(26.8)	Ph			
67	(100)		69	(21.8)	C_3HO_2			
			67	(2.8)	furyl			

[a] L = dibenzoylmethane. [b] L = furoylbenzoylmethane. [c] L = di-(4-fluorbenzoyl)-methane. [d] FPh = fluorophenyl. [e] Each occurring in the $^{58}Ni/^{60}Ni$ isotope ratio.

during 6 h at the same temperature. The solution was stirred for 24 h at room temperature. The colour changed to deep-red. After filtration to remove metallic nickel the toluene and the isomers of cyclooctadiene were removed in vacuo (10^{-3} Torr) and at room temperature. Recrystallization from n-pentane gave analytically pure deep-yellow crystals in better than 70% yield.

Preparation of XXII. 8.6 g (32 mmol) $Ni(cod)_2$; 6.9 g (32.5 mmol) dibenzoylmethane; Yield 9.4 g (24 mmol) XXII = 75%.

Preparation of XXIII. 5.5 g (20 mmol) $Ni(cod)_2$; 4.35 g (20.3 mmol) furoylbenzoylmethane; Yield 6.8 g (17.85 mmol) XXIII = 72%.

Preparation of XXIV. 1.2 g (4.3 mmol) $Ni(cod)_2$; 1.2 g (4.4 mmol) di-4-fluorbenzoylmethane; Yield 1.3 g (3 mmol) XXIV = 70%.

The ^1H NMR data of XXII to XXIV are listed in Table 3, the IR data in Table 4 and the mass spectra in Table 5.

Preparation of the η^3-cyclooctenyl nickel diketonate complexes XXV–XXVIII

The complexes XXV–XXVIII were prepared according to the method of Nüssel [19] involving the reaction of bis-η^3-cyclooctenyl-μ,μ'-dichloro-dinickel with two molar equivalents of the sodium- or thallium-diketonate. Some experimental details for the syntheses of the new complexes XXVI–XXVIII are given below.

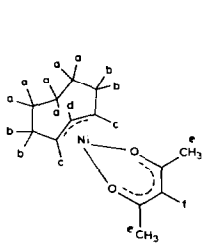
Preparation of XXVI. 1.9 g (4.7 mmol) $[NiBr(\eta^3\text{-}C_8H_{13})]_2$; 1.65 g (9.4 mmol) sodium trifluoroacetylacetonate; Yield 2.1 g (6.5 mmol) XXVI = 80%.

Preparation of XXVII. 1.1 g (2.7 mmol) $[NiBr(\eta^3\text{-}C_8H_{13})]_2$; 2.2 g (5.4 mmol) thallium hexafluoroacetylacetonate; Yield 1.0 g (2.0 mmol) XXVII = 50%, (darkbrown solid, sublimation in vacuo).

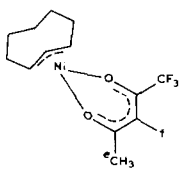
(Continued on p. 389)

TABLE 6

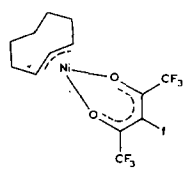
^1H NMR DATA OF THE NICKEL η^3-CYCLOOCTENYL COMPLEXES XXV–XXVIII



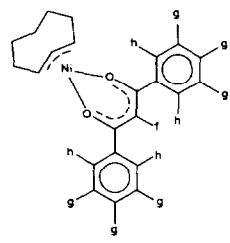
XXV



XXVI



XXVII



XXVIII

Peak asignment	δ(ppm)	Integr.	δ(ppm)	Integr.	δ(ppm)	Integr.	δ(ppm)	Integr.
H_a	1.10–1.50 (m)	6	1.05–1.35 (m)	6	1.35–1.65 (m)	6	1.25–1.60 (m)	6
H_b	1.90–2.15 (m)	4	1.75–2.10 (m)	4	1.95–2.20 (m)	4	2.00–2.40 (m)	4
H_c	3.35–3.70 (qu)	2	3.40–3.70 (qu)	2	3.75–4.10 (qu)	2	3.65–3.90 (qu)	2
H_d	5.40–5.65 (t)	1	5.25–5.45 (t)	1	5.80–6.00 (t)	1	5.75–6.00 (t)	1
H_e	1.80 (s)	6	1.55 (s)	3	–		–	
H_f	5.25 (s)	2	5.65 (s)	1	6.05 (s)	1	6.55 (s)	1
H_g	–		–		–		7.25–7.40 (m)	1
H_h	–		–		–		7.70–7.90 (m)	6
$J_{c,d}$	8.2 Hz		8.0 Hz		7.5 Hz		8.7 Hz	

TABLE 7

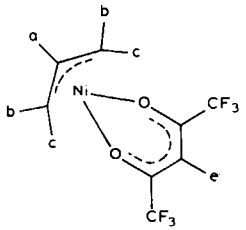
MS DATA OF THE NICKEL-η^3-CYCLOOCTENYL COMPLEXES XXV–XXVIII

XXV [d]		XXVI			XXVII			XXVIII		
m/e	Ion	*m/e*	rel.Int. (%)	Ion	*m/e*	rel.Int. (%)	Ion	*m/e*	rel.Int. (%)	Ion
276	$Ni(C_8H_{13})_2$	364/366	(2.8/1.1)	NiL_2 [a]	472	(2.9)	NiL_2 [b]	390/392	(8.3/5.8)	M^+
266	M^+	320/322	(0.6/0.2)	M^+	374/376	(2.5/1.1)	M^+	282/284	(62.7/27.1)	$M^+ - cod$
256	$Ni(C_5H_7O_2)_2$	211/213	(1.2/0.5)	NiL-H	265/267	(5.8/1.7)	$M^+ - C_8H_{13}$	224	(6.9)	L [c]
218	$(C_8H_{13})_2$	109	(19)	C_8H_{13}	205	(1.3)	L-H	223	(18.4)	L-H
158	$Ni(C_5H_8O_2)$	108	(20)	cod	138	(10.5)	$L-CF_3$	147	(13.8)	L-Ph
109	C_8H_{13}	97	(6)	CF_3CO	110	(8.8)	C_8H_{14}	110	(5.8)	C_8H_{14}
108	C_8H_{12}	84	(48)	$L-CF_3$	109	(26.1)	C_8H_{13}	109	(6.1)	C_8H_{13}
100	$C_5H_8O_2$	67	(100)	C_5H_7	108	(18.3)	cod	108	(6.3)	cod
		66	(47)	CH_3COCH	67	(100)	C_5H_7	105	(31.4)	PhCO
		41	(69)	C_3H_5				77	(55.5)	Ph
								69	(9.9)	C_3HO_2
								67	(78.1)	C_5H_7
								41	(100)	C_3H_5

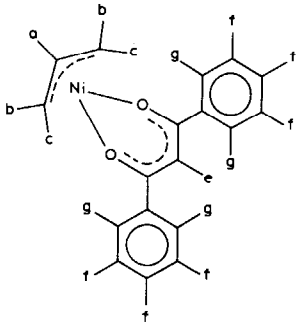
[a] L = trifluoroacetylacetone; [b] L = hexafluoroacetylacetone; [c] L = dibenzoylmethane [d] Data of H.G. Nüssel, Thesis, Bochum 1970.

TABLE 8

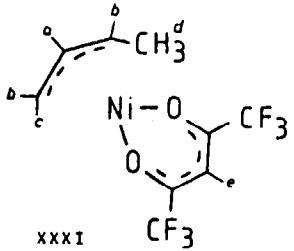
^{1}H NMR DATA OF THE NICKEL η^3-ALLYL AND BUTENYL COMPLEXES XXIX–XXXII



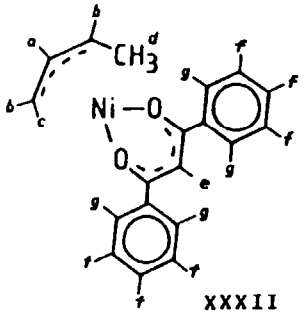
XXIX



XXX



XXXI



XXXII

Peak asignment	δ(ppm)		Integr.	δ(ppm)		Integr.	δ(ppm)		Integr.	δ(ppm)		Integr.
H_a	4.9–5.45	(sept)	1	5.3–5.75	(sept)	1	4.85	(m)	1	5.26	(m)	1
H_b	2.5–2.7	(d)	2	2.65–2.80	(d)	2	2.3–2.5	(m)	2	2.5–2.8	(m)	2
H_c	1.60–1.80	(d)	2	1.85–2.15	(d)	2	1.39	(d)	1	1.79	(d)	1
H_d	–			–			0.27	(d)	3	0.72	(d)	3
H_e	6.08	(s)	1	6.70	(s)	1	6.16	(s)	1	6.75	(s)	1
H_f	–			7.10	(m)	6	–			7.06	(m)	6
H_g	–			7.80	(m)	4	–			7.81	(n)	4

TABLE 9

IR DATA OF THE NICKEL η^3-ALLYL AND BUTENYL COMPLEXES XXIX–XXXII

Peak asignment	IR data (cm^{-1})			
	XXIX	XXX	XXXI	XXXII
=C–H	–	3060	–	3060
–C–H	[a]	2960–2840	[b]	2960–2830
C=C	1648	1595	1647	1595
C–O	1558, 1530	1555, 1505	1555, 1528	1550, 1505
C–C	[a]	1485–1450	[b]	1480–1452
$C-CH_3$	–	–	1378	1371
C–F	1210, 1258	–	1210, 1259	–
NiO	675	682	674	688

[a] IR spectrum recorded in n-pentane. [b] IR spectrum recorded in n-heptane.

Preparation of XXVIII. 1.2 g (2.85 mmol) $[NiBr(\eta^3\text{-}C_8H_{13})]_2$; 2.4 g (5.7 mmol) thallium-1,3-diphenyl-propan-1,3-dionate; Yield 1.1 g (2.8 mmol) XXVIII = 48% (brown micro-crystals).

The ^1H NMR data of the complexes XXV–XXVIII are listed in Table 6 and their MS data in Table 7.

Preparation of the η^3-allyl and butenyl nickel diketonate complexes XXIX–XXXII

Preparation of XXIX. At −70°C 0.95 g (3.51 mmol) η^3-allyl-nickel chlorid was suspended in 30 ml toluene. 7.02 mmol of thallium hexafluoroacetylacetonate in 20 ml toluene were added, leading to an immediate reaction. The colour of the suspenion changed from deep-red to brown yellow. TlCl was removed at −20°C and toluene was evaporated off at −20 to −10°C in vacuo (10^{-2} Torr) to leave pure XXIX. This preparation method can be used to synthesize the complexes XXX to XXXII in about 50% yield.

Preparation of XXX. 1.55 g (5.7 mmol) $[NiCl(C_3H_5)]_2$; 4.8 g (11.4 mmol) thallium-1,3-diphenyl-propan-1,3-dionate.

Preparation of XXXI. 1.60 g (4.2 mmol) $[NiBr(C_4H_7)]_2$; 3.45 g (8.4 mmol) thallium-hexafluoro-acetylacetonate.

Preparation of XXXII. 0.95 g (2.48 mmol) $[NiBr(C_4H_7)]_2$; 2.16 g (4.94 mmol) thallium-1,3-diphenyl-propan-1,3-dionate.

The ^1H NMR data of the complexes XXIX–XXXII are listed in Table 8, the IR data in Table 9 and the MS data in Table 10.

The oligomerization of 1-butene with isolated complexes involved the following general procedure: The reaction was carried out in a 40 ml glass autoclave fitted with a manometer and a valve. The nickel complexes were dissolved in toluene at −10°C and the solution was transferred to the autoclave. After addition of the olefin the solution was stirred at 75–105°C for 1 h. After removal of the unreacted olefin the solution was filtered and analyzed by GLC.

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TABLE 10

MS DATA OF THE NICKEL η^3-ALLYL AND BUTENYL COMPLEXES XXIX–XXXII

XXIX			XXX			XXXI			XXXII		
m/e	rel.Int. (%)	Ion	*m/e*	rel.Int. (%)	Ion	*m/e*	rel.Int. (%)	Ion	*m/e*	rel.Int. (%)	Ion
306/308	(27.8/11.9)	M^+	322/324	(3.9/1.4)	M^+	320/322	(10.5/4.5)	M^+	336/338	(7.2/4.1)	M^+
265	(1)	$M-C_3H_5$	282/284	(40.6/14.7)	HNiL	265	(0.7)	$M-C_4H_7$	282/284	(44.1/15.1)	$M-C_4H_6$
237/239	(8.5/3.8)	$M-CF_3$	283/285	(9.9/3.4)	$M-C_3H_5$	113/115	(52.8/19.6)	M-L[a]	224	(6.7)	L[b] + H
139	(0.8)	L[a]-CF_3	224	(9.5)	L[b]	97	(25.0)	CF_3CO	223	(9.9)	L
99/101	(72.5/29.7)	M-L	223	(21)	L-H	81	(13.4)	C_2F_3	147	(13.3)	L-Ph
98	(22.7)	CF_3COH	147	(22.3)	L-Ph	69	(24.1)	CF_3;C_3HO_2	105	(40.2)	PhCO
97	(14.2)	CF_2CO	105	(100)	PhCO	58/60	(25.5/9.9)	Ni	69	(16.5)	C_3HO_2
69	(24.8)	CF_3;	77	(80.9)	Ph	55	(100)	C_4H_7	58/60	(19.4/5.9)	Ni
		C_3HO_2	69	(7.7)	C_3HO_2				56	(28.5)	C_4H_8
									55	(77.0)	C_4H_7

[a] L = hexafluoroacetylacetone. [b] L = dibenzoylmethane.

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