Oligomerization and Isomerization of Olefins by Catalysts derived from Nickel Complexes of Dithio-β-diketonates‡

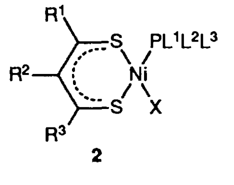
Ramyani Abeywickrema,[a] **Martin A. Bennett,**[a] **Kingsley J. Cavell,***[,b] **Michael Kony,**[b] **Anthony F. Masters***[,c,]† **and Alison G. Webb**[d]
[a] *Research School of Chemistry, Australian National University, Canberra, A.C.T., 2601, Australia*
[b] *Department of Chemistry, University of Tasmania, GPO Box 252C, Hobart, Tasmania, 7001 Australia*
[c] *CSIRO Division of Materials Science and Technology, Locked Bag 33, Clayton, Victoria, 3108, Australia*
[d] *Department of Inorganic Chemistry, University of Sydney, NSW 2006, Australia*

The complexes [Ni{R^{1}C(S)CR^{2}C(S)R^3}$_2$] **1** and [Ni{R^{1}C(S)CR^{2}C(S)R^3}(PL^{1}L^{2}L^3)X] **2** (R, L = alkyl, aryl or CF$_3$; X = Cl, Br or I) have been prepared. The complexes **2** can be chemically anchored to polystyrene or silica–alumina supports *via* pendant phosphine ligands to form the derivatives **3**. The species **2** and **3** in combination with a suitable co-catalyst form extremely active catalysts for the oligomerization of ethylene, propylene or butenes. The immobilised systems show no significant signs of leaching after 24 h operation. In general the oligomerization is highly selective to dimers, however, selectivity and catalyst activity are markedly affected by changes in L. Changes in R affect catalyst activity only.

Catalytic dimerization/oligomerization is a useful method for the conversion of moderately cheap lower molecular weight (*i.e.*, C$_2$–C$_4$) feed olefins into industrially important olefins of higher molecular weight. The use of organometallic complexes in catalysts for this purpose has been widely studied[1–7] and several processes have been commercialised.[8–10] Branched products from the dimerization and co-dimerization of propylene and butylene are suitable as gasoline blending components. Linear products from the dimerization and oligomerization of C$_3$–C$_5$ olefins are desirable for the production of C$_6$–C$_{18}$ plasticiser and detergent range olefins.

We have been seeking new olefin oligomerization catalysts which give improved turnover numbers (*i.e.*, number of converted substrate molecules per active site on the catalyst per unit time) and/or improved selectivity or specificity as to the type or variety of the dimer(s) or oligomer(s) produced from a particular olefin feedstock.

Nickel(II) complexes of the formula [Ni{R^{1}C(S)CR^{2}C(S)R^3}(PL^{1}L^{2}L^3)X] **2** (R, L = alkyl, aryl or CF$_3$; X = Cl, Br or I) containing dithioacetylacetonate (sacsac) or substituted derivatives form extremely active and highly selective catalysts for the oligomerization of lower olefins when activated by an appropriate co-catalyst.



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The compounds [Ni(sacsac)(PEt$_3$)Cl], [Ni{MeC(S)C(CH$_2$-CH=CH$_2$)C(S)Me}(PEt$_3$)Cl] and [Ni(sacsac)(PBu$_3$)Cl] have been reported previously and their crystal structures determined.[11–13]

The air-stable nickel complexes, **2**, form extremely active olefin dimerization catalysts when treated with a suitable co-catalyst. A diversity of activities, stabilities, and product distributions depending on R and L have been observed for the catalytic systems derived from the above complexes.

In preliminary communications, the potential for controlling the catalytic properties by varying the ligand substituents R and L was illustrated using a limited range of substituents.[14–16] We now report more detailed studies exemplifying the control over catalytic properties possible by changing the substituents on the ligands in the nickel precursors **2**. In this paper, we describe the preparation and characterisation of the mixed ligand oligomerization/isomerization catalyst precursors **2**. Several synthetic routes to these complexes are identified. The interconversion of the substituents R^1 and R^3 on the NMR time-scale has been reported previously.[11] The ^{1}H NMR spectra of the complexes are discussed and further evidence for the mechanism for this interconversion is provided. The performance of the compounds **2** as olefin oligomerization and isomerization catalyst precursors is also described. The demonstration of the control of catalytic activity and selectivity by the substituents R and L has involved the syntheses of several new derivatives which are described herein.

Results and Discussion

Syntheses of β*-Diketones.*—The syntheses of the β-diketones were relatively straightforward and followed established procedures. The two general methods were reaction of Na(acac) (acac = acetylacetonate) with an alkyl halide to introduce substituents R^2, and reaction of an alkylmethyl ketone with sodium hydride, followed by condensation with an alkylethyl ester to introduce the substituents R^1 and R^3. The β-diketones were obtained as high-boiling point liquids or low-melting point solids (Table 1). We have previously compared the mass spectra of β-diketones and their monothio analogues.[17] The mass spectra of the present β-diketones are analogous to that of dipivaloylmethane.[17] The ^{1}H and ^{13}C NMR parameters of a typical derivative, MeC(O)CH(C$_{16}$H$_{33}$)-C(O)Me, are included in the Experimental section.

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† *Present address:* Department of Inorganic Chemistry, University of Sydney, NSW, 2006, Australia

‡ *Non-SI units employed:* Torr ≈ 133 Pa, lbf in^{-2} ≈ 6895 Pa.

Table 1 Analytical data

Compound	Colour	Analysis (%)[a]					
		C	H	S	Cl	P	F
$MeC(O)CH(C_{16}H_{33})C(O)Me$	—	77.60 (77.70)	12.70 (12.40)				
$[Ni\{PhC(S)CHC(S)Ph\}_2]$	Dark green	56.95 (57.50)	5.50 (5.25)	25.3 (25.6)			
$[Ni\{MeC(S)CHC(S)C_7H_9\}_2]$	Dark green	55.35 (55.35)	5.55 (5.50)	26.4 (26.9)			
$[Ni\{MeC(S)CHC(S)CF_3\}_2]$	Dark green	27.90 (28.00)	2.20 (1.90)	29.2 (29.90)			26.8 (26.55)
$[Ni\{MeC(S)C(CH_2CH{=}CH_2)C(S)Me\}]$	Dark green	47.60 (47.90)	5.35 (5.35)	31.70 (31.70)			
$[Ni\{MeC(S)C(CH_2CH_2CH{=}CH_2)C(S)Me\}_2]$	Dark green	49.45 (50.35)	6.10 (6.10)	29.9 (29.85)			
$[Ni\{MeC(S)C(CH_2CH{=}CH_2)C(S)Me\}(PEt_3)Cl]$	Dark red	44.05 (43.85)	6.70 (6.85)	16.9 (16.70)	9.0 (9.25)	7.9 (8.05)	
$[Ni\{MeC(S)CHC(S)Me\}\{P(C_6H_{11})_3\}Cl]$	Dark red	52.75 (54.60)	8.30 (7.95)	12.6 (12.7)			
$[Ni\{MeC(S)C(CH_2Ph)C(S)Me\}(PBu_3)Cl]$	Dark green	55.35 (55.65)	7.65 (7.80)	12.7 (12.40)	6.9 (6.85)	6.1 (6.00)	
$[Ni\{Bu^tC(S)CHC(S)Bu^t\}(PBu_3)Cl]$	Dark red	54.15 (53.95)	9.05 (9.05)	12.8 (12.55)	7.0 (6.95)	6.2 (6.05)	
$[Ni\{MeC(S)CHC(S)CF_3\}(PEt_3)Cl]$	Dark green	33.45 (33.25)	5.20 (4.80)	15.4 (16.1)	7.7 (8.9)	7.8 (8.1)	14.35 (13.90)
$[Ni\{MeC(S)CHC(S)Me\}(PPh_3)Cl]$	Dark	56.70 (56.65)	4.55 (4.55)	12.7 (13.2)	7.1 (7.3)	6.4 (6.4)	
$[Ni\{MeC(S)CHC(S)CF_3\}(PBu_3)Cl]$	Dark	42.10 (42.40)	6.45 (6.50)	12.9 (13.30)	7.0 (7.35)	6.4 (6.45)	12.2 (11.85)
$[Ni\{MeC(S)CHC(S)Me\}\{P(C_{14}H_{29})_3\}Cl]$	Dark red	65.65 (66.75)	10.65 (10.85)	7.8 (7.6)	3.7 (4.2)	3.8 (3.7)	
$[Ni\{MeC(S)CHC(S)Me\}\{P(C_{16}H_{33})_3\}Cl]$	Dark red	67.95 (68.25)	11.75 (11.45)				
$[Ni\{MeC(S)CHC(S)Me\}(PEt_3)I]$	Dark red-purple	30.70 (30.35)	4.95 (5.1)				
$[Ni\{MeC(S)CHC(S)Me\}(PPh_3)I]$[b]	Dark brown	48.25 (47.70)	3.90 (3.85)				
$[Ni\{MeC(S)CHC(S)Me\}(PBu_3)Br]$[c]	Dark brown	43.55 (43.25)	7.00 (7.25)	13.3 (13.60)		6.7 (6.55)	

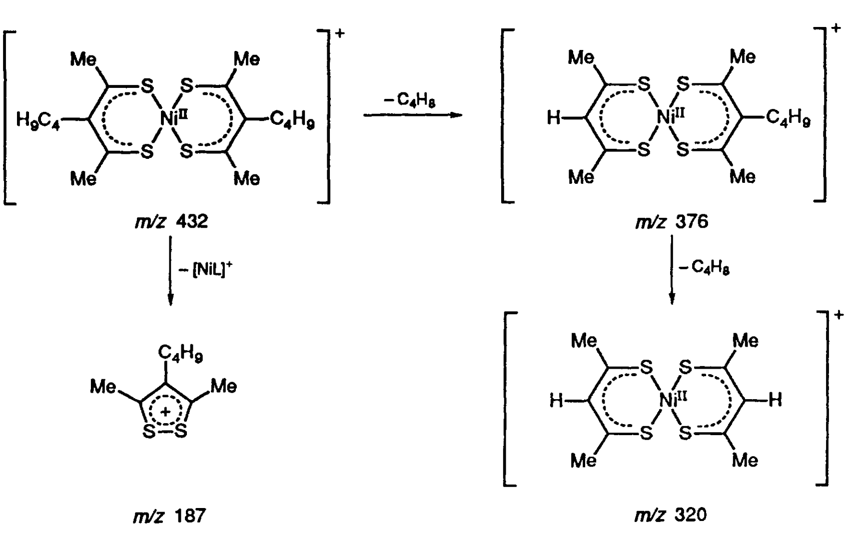
[a] Calculated values in parentheses. [b] I, 5.25 (5.35%). [c] Br, 16.9 (16.90%).

Syntheses of Bis(dithio-β-diketonato)nickel(II) *Compounds* **1**.—A particular virtue of catalysts derived from the compounds **2** is the potential rationally to control such operational parameters as activity, selectivity, solubility, *etc.*, by varying the substituents R and L on the compounds **2**.[14–16] The control of catalytic activities and selectivities by variation of phosphine substituents is well known,[2] and a wide variety of substituted phosphines is commercially available. Keim has illustrated the effects of varying β-diketonate substituents in $[Ni(\eta^3\text{-}C_8H_{13})(\beta\text{-diketonate})]$ complexes on catalytic activity and X-ray photoelectron chemical shifts.[18] Few, if any, catalytic systems have the potential for such systematic and extensive catalyst fine tuning by substituent variation as do those derived from the species **2**. However, the realisation of this potential requires an extension of the small range of nickel bis(dithio-β-diketonates) beyond that known at the commencement of this study. The successful syntheses of $[Ni\{R^1C(S)CR^2C(S)R^3\}_2]$ **1** with R^2 = allyl, benzyl, butyl or hexadecyl, all with $R^1 = R^3$ = methyl, and of the compounds with R^1 = norbornenyl, R^3 = methyl and with R^1 = octyl, R^3 = heptyl (Table 1), demonstrate that bulky substituents can be incorporated at all positions around the chelate ring and that asymmetric substitution of the chelate ring is easily achieved. The compounds have been characterized by elemental analyses and spectroscopically. All can be prepared in good yields (43–66%) and in high purity. The NMR spectra of these compounds are as expected. The mass spectra of $[M\{R^1C(S)CR^2C(S)R^3\}_n]$ (n = 2 or 3) compounds in general[17] are dominated by the oxidised ligands, with very few metal-containing ions being observed. Even $[Ni\{Bu^tC(S)CHC(S)Bu^t\}_2]$ has few, if any, metal-containing ion peaks other than the molecular ion peak in its mass spectrum. In contrast, the mass spectra of both $[Ni\{MeC(S)CBuC(S)CMe\}_2]$ and $[Ni\{C_8H_{17}C(S)CHC(S)C_7H_{15}\}_2]$ show peaks due to metal-containing ions derived from the molecular ion (*e.g.*, Scheme 1). Both mass spectra, however, conform to the generalisation reported earlier in that they are dominated by peaks due to the appropriate 1,2-dithiolylium ions.

Syntheses of Halogeno(dithio-β-diketonato)nickel Phosphine Complexes **2**.—The complexes $[Ni\{R^1C(S)CR^2C(S)R^3\}(PL^1L^2L^3)X]$ **2** were prepared principally by a metathetical ligand exchange reaction between $[Ni\{R^1C(S)CR^2C(S)R^3\}_2]$ and $[Ni(PL^1L^2L^3)_2X_2]$ in refluxing benzene, based on the method of Fackler and Masters[11] [equation (1)].

$$[Ni\{R^1C(S)CR^2C(S)R^3\}_2] + [Ni(PL^1L^2L^3)_2X_2] \longrightarrow 2[Ni\{R^1C(S)CR^2C(S)R^3\}(PL^1L^2L^3)X] \quad (1)$$

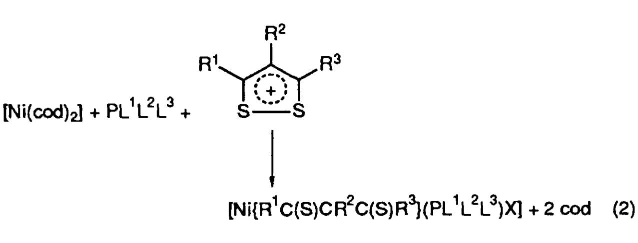
Yields of between 52 and 91% were obtained by this method. The ligand X is also easily varied by this method if the appropriate $[Ni(PL^1L^2L^3)_2X_2]$ is available. Thus, for example, both $[Ni(sacsac)(PBu_3)X]$ (X = Cl or Br) were prepared by this route. For the preparation of the complex $[Ni(sacsac)(PPh_3)Cl]$ it was found that better yields were obtained if the reflux time was shortened to between 45 and 60 min. However, as apparent from their molecular structures,[12,13] even in the simplest of the



Scheme 1

complexes there is a significant steric interaction around the crowded nickel centre. As a consequence, complexes containing bulky phosphine ligands, *e.g.*, PPh_3, $P(C_6H_{11})_3$, *etc.*, are not as readily prepared by the metathetical route and where the desired product has been isolated, yields have been relatively low. There appears to be an optimum temperature and reaction time above which no increase in the yield of reaction (1) is obtained. This observation is particularly evident when the preparations of $[Ni\{R^1C(S)CR^2C(S)R^3\}(PPh_3)X]$ derivatives are attempted. In this case the maximum temperature is that of boiling benzene and the optimum reflux time is approximately 1 h. Increasing the temperature or heating time leads to decomposition and a decreased yield of the desired complex. The amount of unreacted $[Ni\{R^1C(S)CR^2C(S)R^3\}_2]$ is significant, and is generally some 40%. A similar situation pertains in the syntheses of $P(C_6H_{11})_3$ complexes.

The preparation of complexes containing bulky phosphine ligands is highly desirable. Catalysts derived from such species have been shown, for other systems, to exhibit drastically altered catalytic behaviour.[2] In the current systems, incorporation of the ligands PPh_3 and $P(C_6H_{11})_3$ has led to significant changes to catalyst stability, activity and product distribution (see below). To attempt to overcome the problems associated with preparing complexes containing bulky phosphines, a second approach was developed. This method involved the oxidative addition of a dithiolylium salt to a suitable source of zero-valent nickel (*e.g.*, $[Ni(cod)_2]$, cod = cycloocta-1,5-diene) in the presence of an appropriate amount of the selected phosphine [equation (2)].



(2)

The complexes $[Ni(sacsac)(PEt_3)I]$, $[Ni(sacsac)(PPh_3)I]$ and $[Ni(sacsac)\{P(C_6H_{11})_3\}I]$ were prepared in this manner. For the preparation of $[Ni(sacsac)(PEt_3)I]$ by reaction (2) a slight excess of phosphine was employed, however for the bulky phosphines, *e.g.*, PPh_3 and $P(C_6H_{11})_3$, large excesses of phosphine were required, *i.e.*, a reactant ratio of nickel(0) complex : dithiolylium iodide : phosphine of 1 : 1 : 4–5 was necessary. In all preparations, $[Ni(sacsac)_2]$ formed as a by-product, the amount of which appeared to depend on the bulk of the phosphine.

The yield obtained by the oxidative addition method ($\approx 50\%$) for the $[Ni(sacsac)(PEt_3)X]$ complex was somewhat lower than that obtained by the metathesis approach ($\approx 80\%$). However, for the bulkier phosphines the oxidative addition leads to slightly improved yields. Although this route has been exemplified for the iodo complexes, it is presumably suitable for the preparation of compounds **2** with other ligands X (*e.g.*, X = Br). Dithiolylium cations certainly undergo oxidative additions to other metals.[19,20] The 3,5-dimethyl-1,2-dithiolylium cation is accessible in reasonable yield as its iodide salt and in lower yields as its bromide salt.[21] Additionally, the bromide salt is less stable than the iodide salt and decomposes on storage. Thus, for derivatives **2** with X = Br, the metathetical route [equation (1)] is preferred, unless the phosphine is bulky.

We have also described a route to the complexes **2** directly from $[Ni\{R^1C(S)CR^2C(S)R^3\}_2]$ **1**, the appropriate phosphine and a nickel salt [reaction (3)].[22]

$$[Ni\{R^1C(S)CR^2C(S)R^3\}] + 2PL_3 + NiCl_2{\cdot}6H_2O \longrightarrow$$
$$2[Ni\{R^1C(S)CR^2C(S)R^3\}(PL_3)Cl] + 6H_2O \quad (3)$$

The proton NMR spectra in $CDCl_3$ (probe temperature 25 °C) of the complexes $[Ni(sacsac)(PL^1L^2L^3)X]$ show a single peak for the two inequivalent sets of methyl protons, indicating that the methyl groups are magnetically equivalent on the NMR timescale at this temperature. However, two peaks are resolved at lower temperatures. To explain this result a ligand dissociation mechanism involving either the halide or phosphine has been proposed.[11] Based on the following observations, we propose that it is halide dissociation and reassociation that is the cause of the methyl group equivalence. The complex $[Ni(sacsac)(PEt_3)I]$, which contains a small phosphine and a relatively strongly complexing halide, exhibits a doublet for the methyl protons at 20 °C. However, the iodide complex containing the bulky phosphine, PPh_3, which would have the effect of assisting halide displacement, has a singlet in the methyl region at this temperature.

Furthermore, at 100 MHz in CD_2Cl_2, the methyl region of the $[Ni(sacsac)(PEt_3)Cl]$ ^1H NMR spectrum has two singlets (δ 2.40, 2.25) for which the coalescence temperature is approximately 25 °C[11] (as expected, no coalescence is detected at 25 °C at 400 MHz). However, when a polar solvent is added (*e.g.*, for a solvent mixture of 95% CD_2Cl_2–5% CD_3OD) coalescence occurs at approximately 16 °C. In a 1:1 mixture of CD_2Cl_2–CD_3OD the coalescence temperature was lowered still further to approximately −10 °C. Assuming the same mechanism applies in the different solvents, such behaviour suggests the

Table 2 Phosphorus-31 NMR chemical shifts for the complexes [Ni{$R^1C(S)CR^2C(S)R^3$}(PL_3)X]

$R^1C(S)CR^2C(S)R^3$	PL_3	X	δ(^{31}P)
MeC(S)CHC(S)Me	PBu_3	Cl	9.8
MeC(S)C($CH_2CH{=}CH_2$)C(S)Me	PBu_3	Cl	10.0
MeC(S)C(CH_2Ph)C(S)Me	PBu_3	Cl	10.23
Bu^{t}C(S)CHC(S)Bu^t	PBu_3	Cl	10.81
MeC(S)CHC(S)CF_3	PBu_3	Cl	12.62
MeC(S)CHC(S)Me	PEt_3	Cl	17.19*
MeC(S)CHC(S)Me	PEt_3	I	18.38
MeC(S)CHC(S)Me	PEt_3	I	18.38
MeC(S)CHC(S)Me	PPh_3	I	30.25
MeC(S)CHC(S)Me	$P(C_6H_{11})_3$	I	31.17

* Ref. 11.

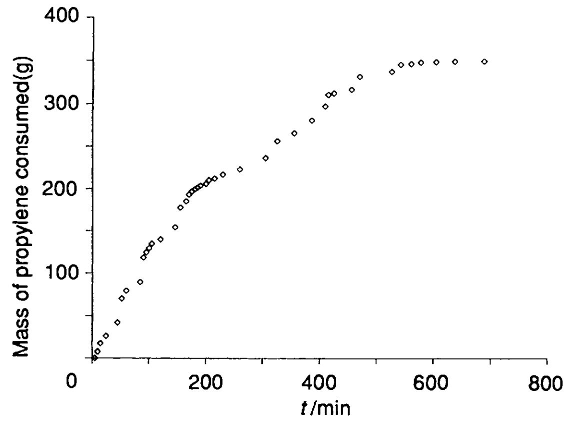


Fig. 1 Propylene consumption with time for the catalyst system [Ni(sacsac)(PBu_3)Cl] + $AlEt_2Cl$. Reaction conditions: 0 °C, constant propylene pressure of 0.5 lbf in^{-2}, chlorobenzene solvent; employing closed test rig method

dissociation process is favoured by a polar solvent, in turn suggesting that charged or polar species (*e.g.*, [Ni(sacsac)(PEt_3)]$^+$X$^-$) are produced in the equilibration process.

The anticipated transmission of substituent effects through these molecules is conveniently illustrated by their ^{31}P NMR spectra. Thus, the ^{31}P NMR chemical shifts of several [Ni{$R^1C(S)CR^2C(S)R^3$}(PL_3)X] derivatives are sensitive to the nature of all of the ligands (Table 2). A related dependence of nickel electron spectroscopy for chemical analysis (ESCA) chemical shifts on β-diketone substituents in [Ni(η^3-C_8H_{13})(β-diketonate)] complexes has been observed.[18]

Syntheses of Phosphinated Supports.—The concept of combining the best features of homogeneous and heterogeneous catalysts by chemically anchoring homogeneous catalysts to inert supports has received considerable attention.[23–26] In the present study, the compounds **2** were chemically anchored to high surface area silica–alumina or to polystyrene beads *via* phosphine ligands grafted onto these supports. In the case of the silica–alumina support, the species **2** could be anchored to the phosphine either before or after the phosphine was grafted to the support.

The surface area of the polystyrene beads decreased during the functionalisation process. A comparison of XPS (X-ray photoelectron spectroscopy) and elemental analyses on the brominated polystyrene beads demonstrated that the bromination occurred preferentially at the surface of the beads. This effect was particularly noticeable at high levels of bromination of more highly cross-linked polystyrene beads.

Syntheses of Compounds anchored to Phosphinated Supports.—The complexes **2** could be anchored to insoluble supports *via* their phosphine ligands to form surface-confined species **3** by two methods. One was ligand exchange, carried out by stirring together phosphinated silica–alumina or phosphinated polystyrene beads and a solution of [Ni(sacsac)(PPh_3)Cl] at room temperature in toluene or tetrahydrofuran, respectively [equation (4)]. The other route to complexes **3**

$$\text{support–PPh}_2 + [\text{Ni(sacsac)(PPh}_3\text{)Cl}] \longrightarrow [\text{Ni(sacsac)(support–PPh}_2\text{)Cl}] + \text{PPh}_3 \quad (4)$$

was the interaction of the support material with a nickel complex containing a phosphine with a functional group able to react with the hydroxyl groups on the support. Thus, the complex [Ni(sacsac){$Ph_2PCH_2CH_2Si(OEt)_3$}Cl] was treated with silica–alumina (sil) in refluxing benzene or toluene to yield a deep purple solid [equation (5)]. The supported complex

$$\text{sil} + [\text{Ni(sacsac)\{Ph}_2\text{PCH}_2\text{CH}_2\text{Si(OEt)}_3\text{\}Cl}] \longrightarrow [\text{Ni(sacsac)(sil–O}_3\text{SiCH}_2\text{CH}_2\text{PPh}_2\text{)Cl}] + 3\text{EtOH} \quad (5)$$

[Ni(sacsac)(sil–$O_3SiCH_2CH_2PPh_2$)Cl] was prepared by both routes.

Catalytic Experiments.—Catalysts derived from the species **2** and $AlEt_2Cl$ are highly active for olefin oligomerization and isomerization. These catalysts may be used in either homogeneous or heterogeneous systems. No catalytic activity was observed under the same experimental conditions using either **2** or $AlEt_2Cl$ alone. Similarly, no catalytic activity was observed using combinations of [Ni(sacsac)$_2$] and $AlEt_2Cl$ or [Ni(sacsac)$_2$], $AlEt_2Cl$ and PPh_3.

The choice of co-catalyst appears very important as no oligomerization activity was observed for [Ni(sacsac)(PR_3)Cl] systems when $AlEt_3$ or $AlEt_2(OEt)$ was used instead of $AlEt_2Cl$. Furthermore, contamination of the $AlEt_2Cl$ with $AlEt_3$ resulted in reduced activity. The effectiveness of a range of potential co-catalysts has been discussed previously.[27] Tables 3 and 4 present the results of catalytic testing carried out using the flow-through system. Catalytic activities using this approach were considerably lower than when the closed test apparatus was employed. Lower activities are thought to be due to inadequate mixing and to diffusion limitations. However, Tables 3 and 4 illustrate the effects of varying the ligand substituents on the catalyst activity and product distribution, respectively. In these examples propylene was used as the olefin feed. According to the commonly accepted mechanism of transition-metal catalysed olefin oligomerization, there are twelve possible C_6 isomers obtained directly or by double-bond shift isomerization. Of these we observe and can identify ten. The remaining two are probably present in amounts too small to be observed and/or are obscured by other peaks in the gas chromatography trace.

Results from catalytic testing using the closed system are listed in Table 5, clearly demonstrating the increased catalytic activity under these conditions, even allowing for the increased temperature of testing (0 °C compared to −15 °C for the flow method). Product distributions obtained from the closed system were not significantly different to those obtained previously. A typical propylene consumption plot obtained directly from the output of the top-loading balance is shown in Fig. 1 and the resulting activity *versus* time plot is shown in Fig. 2. Features include a brief induction period followed by a period of steady catalyst deactivation and then a long period of almost steady activity—catalyst deactivation during this period is slow. Finally, there is a period of increased activity followed by rapid deactivation, which occurs when there has been significant product build-up in solution.[28] Coinciding with this deactivation a precipitate is evident in the solution. It is possible that the rapid deactivation is due to insolubility of the catalyst in what is at that stage a predominantly organic solvent.[28]

It has been shown that the activities of other propylene dimerization systems are solvent dependent, best results having been obtained in solvents such as chlorobenzene or dichloromethane.[2,5,21] Table 3 indicates that the propylene oligomerization rates for our catalysts are considerably higher in chlorobenzene than in toluene. Complexes **2** with suitable solubilizing substituents R or L also function quite satisfactorily in neat olefin or alkane solvents. In the example shown in Fig. 3, $[\mathrm{Ni(sacsac)\{P(C_{14}H_{29})_3\}Cl}]$ was employed as the catalyst precursor. There is an 'induction' period of lower activity, followed by a long period of near constant activity. The 'induction' period is considerably longer in this example than is generally observed in toluene or chlorobenzene. Why this is so is unclear. Fig. 3 also demonstrates the longevity and stability of the catalyst, and that the olefin flow can be interrupted and restarted without loss in activity. During this experiment the propylene flow was discontinued for 14 h and the closed reaction vessel was maintained at 0 °C over this period. On re-initiating the propylene flow the catalyst continued turning over with the same activity as evident previously. (These catalysts are, however, unstable in the absence of olefin.)

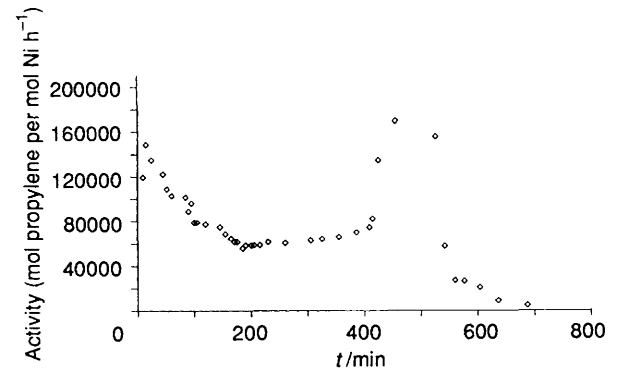


Fig. 2 Plot showing the change in activity with time for the experiment illustrated in Fig. 1

Table 3 Effect of changing ligands on catalyst activity

Catalyst[a]	Turnover number [mol C_3H_6 converted (mol Ni)$^{-1}$ h^{-1}]
$[\mathrm{Ni(sacsac)(PEt_3)Cl}]$	3 500
	17 300[b]
$[\mathrm{Ni(sacsac)(PBu_3)Cl}]$	6 000
	37 000[b]
$[\mathrm{Ni(sacsac)(PPh_3)Cl}]$[c]	> 30 000[b]
$[\mathrm{Ni(sacsac)\{P(OEt)Ph_2\}Cl}]$	3 000[b]
$[\mathrm{Ni(sacsac)\{P(C_6H_{11})_3\}Cl}]$	10 500[b]
$[\mathrm{Ni\{MeC(S)CHC(S)CF_3\}(PBu_3)Cl}]$	13 000
$[\mathrm{Ni\{MeC(S)C(CH_2CH{=}CH_2)C(S)Me\}(PEt_3)Cl}]$	4 000
$[\mathrm{Ni\{MeC(S)C(CH_2CH{=}CH_2)C(S)Me\}(PBu_3)Cl}]$	2 200
$[\mathrm{Ni\{Bu^tC(S)CHC(S)Bu^t\}(PBu_3)Cl}]$	21 300
$[\mathrm{Ni\{MeC(S)C(CH_2Ph)C(S)Me\}(PBu_3)Cl}]$	5 800
$[\mathrm{Ni(sacsac)(polystyrene{-}PPh_2)Cl}]$	350
$[\mathrm{Ni(sacsac)(sil{-}O_3SiCH_2CH_2PPh_2)Cl}]$[d]	25
$[\mathrm{Ni(sacsac)(sil{-}O_3SiCH_2CH_2PPh_2)Cl}]$[e]	2 500

[a] Reaction conditions: *ca.* 2 × 10^{-5} mol of nickel complex, *ca.* 5 × 10^{-4} mol of $\mathrm{AlEt_2Cl}$ dissolved in 50–60 g of toluene saturated with propylene at −14 ± 1 °C with a flow of propylene such as to ensure a saturated solution at all times. [b] Chlorobenzene as solvent. [c] After 5 min of operation. This catalyst rapidly deactivates. It has a half-life of approximately 30 min. [d] Prepared by exchanging $[\mathrm{Ni(sacsac)(PPh_3)Cl}]$ with phosphinated silica–alumina. [e] Prepared by treating $[\mathrm{Ni(sacsac)\{Ph_2PCH_2CH_2Si(OEt)_3\}Cl}]$ with silica–alumina.

The observation that activated catalyst systems appear stable for long periods of time with no substrate gas flowing suggests that the slow deactivation process often noted for these catalysts is caused by trace impurities present in the feed or that there is some secondary- or side-reaction which only proceeds in the presence of fresh feed. The latter is less likely as the catalysts are stable in the presence of product olefin, which they continue to isomerize or very slowly oligomerize further without apparent deactivation.

For a common catalyst system, the rate of ethylene oligomerization was greater than that of propylene oligomerization, which in turn was substantially greater than that of butene oligomerization, as expected from thermodynamic considerations.[29] No hexene oligomerization was observed in these experiments.

The catalysts are extremely active double-bond shift olefin isomerization catalysts. The conversion of hex-1-ene to its internal isomers is essentially complete within 5 min. A crude estimate of the hexene isomerization activity shows it to

Table 5 Catalytic activity using closed test rig

Catalyst[a]	Turnover number [mol C_3H_6 converted (mol Ni)$^{-1}$ h^{-1}]
$[\mathrm{Ni(sacsac)(PMe_3)Cl}]$	2 300
$[\mathrm{Ni(sacsac)(PBu_3)Cl}]$	130 000
$[\mathrm{Ni(sacsac)\{P(C_{14}H_{29})_3\}Cl}]$	20 000[b]
	9 000[c]
	16 500
$[\mathrm{Ni\{MeC(S)CHC(S)C_7H_9\}(PBu_3)Cl}]$	52 000

[a] Reaction conditions: *ca.* 2 × 10^{-5} mol of nickel complex, *ca.* 5 × 10^{-4} mol of $\mathrm{AlEt_2Cl}$ dissolved in 50–60 g of chlorobenzene with a constant pressure of approximately 0.5 lbf in^{-2} propylene in a closed system at 0 ± 1 °C. [b] Oct-1-ene as solvent. [c] Heptane as solvent.

Table 4 Effects of changing ligands on product distribution

	Dimer cut			
Catalyst precursor	Dimethylbutenes	Methylpentenes	*n*-Hexenes	Higher oligomers
$[\mathrm{Ni(sacsac)(PEt_3)Cl}]$	26	67	7	1–2
$[\mathrm{Ni(sacsac)(PBu_3)Cl}]$	29	67	4	4–5
$[\mathrm{Ni\{MeC(S)CHC(S)CF_3\}(PBu_3)Cl}]$	26	69	5	2
$[\mathrm{Ni\{MeC(S)C(CH_2CH{=}CH_2)C(S)Me\}(PEt_3)Cl}]$	24	70	6	—
$[\mathrm{Ni\{MeC(S)C(CH_2CH{=}CH_2)C(S)Me\}(PBu_3)Cl}]$	25	69	6	< 1
$[\mathrm{Ni\{Bu^tC(S)CHC(S)Bu^t\}(PBu_3)Cl}]$	27	69	4	2
$[\mathrm{Ni\{MeC(S)C(CH_2Ph)C(S)Me\}(PBu_3)Cl}]$	28	69	3	—
$[\mathrm{Ni(sacsac)(PPh_3)Cl}]$	10	74	16	—
$[\mathrm{Ni(sacsac)\{P(C_6H_{11})_3\}Cl}]$	76	23	1	
$[\mathrm{Ni(sacsac)\{P(OEt)Ph_2\}Cl}]$	8	72	20	—
$[\mathrm{Ni(sacsac)\{P(C_{14}H_{29})_3\}Cl}]$	17	73	10	
$[\mathrm{Ni(sacsac)(polystyrene{-}PPh_2)Cl}]$	10	82	8	4
$[\mathrm{Ni(sacsac)(sil{-}O_3SiCH_2CH_2PPh_2)Cl}]$ *	8	83	9	7

* Prepared by treating $[\mathrm{Ni(sacsac)\{Ph_2PCH_2CH_2Si(OEt)_3\}Cl}]$ with silica–alumina.

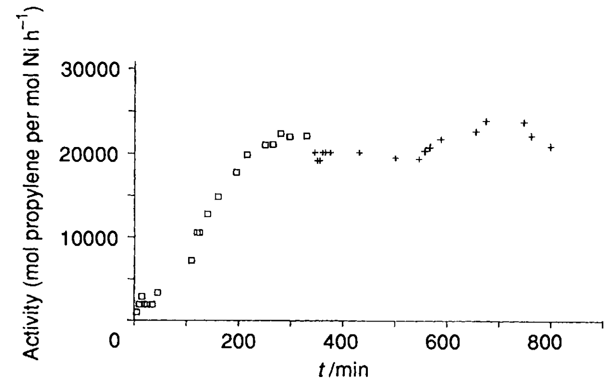


Fig. 3 Operation of the catalyst systems [Ni(sacac){P($C_{14}H_{29}$)$_3$}-Cl] + $AlEt_2Cl$ in pure alkene solvent. Reaction conditions: 0 °C, constant propylene pressure of 0.5 lbf in^{-2} oct-1-ene solvent. (□) Activity *vs.* time plot, day 1. (+) Activity *vs.* time plot, day 2

Table 6 Operation of anchored catalyst

Description	Total C_3H_6 converted/mol[a]	Catalyst activity[b]
System before separation of supernatant and solid (after 120 min operation)	0.2760	2500
Supernatant only (90 min after recommencement of propylene flow)	0.2752[c]	0
Solid catalyst		
5 min after recommencement	0.0102	2500
145 min after recommencement	0.2740	2300

[a] Calculated from the total amount of dimers and higher oligomers detected in solution by gas chromatographic analysis. [b] Mol C_3H_6 converted per mol Ni per hour. [c] The supernatant contains all oligomers produced in the first stage of the experiment. The data show that no further propylene oligomerization was detected.

be about an order of magnitude greater than propylene oligomerization. The hexene isomerization product distribution approaches, but is significantly different from, the equilibrium thermodynamic isomer distribution.[28]

In order to establish whether there was any observable interference in the isomerization process caused by the oligomerization reaction, *i.e.*, whether isomerization is competitive with oligomerization under the conditions of our experiments, hex-1-ene was added to a catalyst that was already oligomerizing propylene. Essentially all of the added hex-1-ene had been isomerized within 5 min. No fluctuation in oligomerization activity was detected. Thus, the isomerization of hex-1-ene to the various internal isomers is extremely rapid even in the presence of propylene. It is possible that the isomerization of the *trans* internal olefins to their *cis* counterparts has been slowed by the oligomerization process. However, the presence of the various hexene isomers produced separately in the dimerization of propylene makes any conclusion drawn from the relative amounts of the internal isomers uncertain.

Chemically anchored complexes also give rise to active catalysts (Table 3). In particular, the substance prepared by interacting [Ni(sacsac){$PPh_2CH_2CH_2Si(OEt)_3$}Cl] with silica–alumina, when combined with $AlEt_2Cl$ produces a catalyst with an activity comparable to the less active of the homogeneous catalysts. In contrast, the supported complex prepared by exchanging [Ni(sacsac)(PPh_3)Cl] with phosphinated silica–alumina gives rise to a significantly less active catalyst. Substantial phosphine oxide formation has been shown to accompany the reaction of $(EtO)_3SiCH_2CH_2PPh_2$ with silica prior to complex formation and may explain the considerably lower activities of catalysts prepared by this route.[30,31] Complexation of the phosphine anchor to the nickel centre prior to the immobilisation reaction with silica–alumina may inhibit phosphine oxide formation.

The catalyst derived from [Ni(sacsac)(PPh_3)Cl] and phosphinated polystyrene also has a low activity. In this case, the nickel precursor is supported on highly cross-linked (>50%) polystyrene. The low activity of the catalyst may derive from diffusion limitations on reagent penetration of the highly cross-linked resin under the experimental conditions. Hence much of the nickel may be inaccessible for reaction. Elemental X-ray analysis of a cleaved polymer bead showed the nickel to be distributed throughout the polymer.

A comparison of the product distributions for heterogeneous and homogeneous catalysts (Table 4) shows consistent behaviour. For homogeneous systems based on complexes of the type [Ni(sacsac)(PPh_2R)Cl], where R is a non-sterically demanding group (*e.g.*, OEt or $CH_2CH_2CO_2CH_2CH_3$) the product distributions are very similar to that observed for the immobilised catalysts in which the phosphine also has the PPh_2R moiety. These systems give rise to a greater amount of less-branched products. In particular there is a large increase in the percentage of methylpentenes produced, at the expense of the more highly branched dimethylbutenes.

To establish the stability of the nickel–phosphorus bond and to determine whether catalyst was leached from the support during catalytic operation, the supported sample derived from [Ni(sacsac){$Ph_2PCH_2CH_2Si(OEt)_3$}Cl] immobilised on silica–alumina was tested in the normal manner using propylene as the feed olefin and toluene as the solvent. Aliquots were taken at intervals and analysed in the usual way. After 2 h of operation, the supernatant was removed from the still highly coloured solid and transferred to a second reaction vessel held at −15 °C. The solid was carefully washed, the solid and reaction vessel were stored at −20 °C until required and the washings were added to the supernatant. The flow of pure propylene was then restored and the system operated as in a normal test experiment. After a further 90 min of operation, an aliquot was taken and analysed. No detectable activity resided with the liquid phase, *i.e.*, no active catalyst was leached from the support.

The solid supported catalyst was brought to −15 °C and washed three times with 15 cm^3 aliquots of cold, degassed dry toluene and the washings discarded. Cold (−15 °C) toluene and a small amount of fresh co-catalyst were added to the solid and the propylene flow re-initiated. Aliquots were removed for analysis 5 and 145 min after the passage of propylene was recommenced.

Results for each stage of the experiment are given in Table 6 which shows that within experimental error, all catalytic activity for propylene oligomerization is associated with the solid supported catalyst. No activity had been lost by catalyst leaching or by other processes, *i.e.*, the nickel–phosphorus bond remains intact throughout the catalyst initiation and operation.

The behaviour of the immobilised catalysts provides some insight into the nature of the active species. The stability of the nickel–phosphorus bond suggests that the active species contains a strongly bound phosphorus ligand. This is in agreement with the observation that changing L has a marked effect on both activity and product distribution.

The effect of the ligand X in the precursors **2** was probed by comparing the performance of compounds [Ni(sacsac)-(PBu_3)X] (X = Cl or Br) using the flow-through operation mode, method (1). Fig. 4 illustrates several experiments with the two precursors under identical conditions. Under these conditions, no significant difference in catalytic performance could be detected.

The R groups on the dithio-β-diketonate ligands markedly influence activity, suggesting that the dithio-β-diketonate ligands are also associated with the active species. This leaves the halide as the labile ligand on activation of the complexes. This proposal is consistent with the suggested lability of the halide as discussed previously.[11] Based on these considerations,the intermediate **I** is thought likely to be involved in

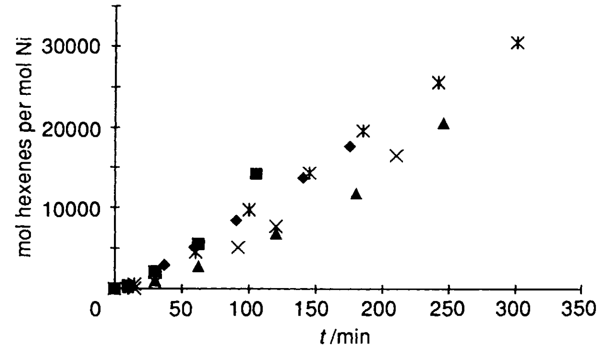
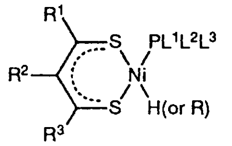
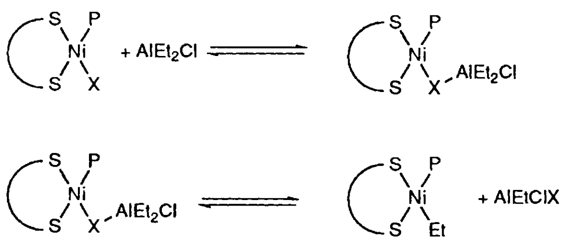


Fig. 4 Operation of the catalyst systems [Ni(sacsac)(PBu_3)X] + $AlEt_2Cl$ (X = Cl or Br). Reaction conditions: −14 °C, propylene feed, toluene solvent, employing flow-through method 1. Initial nickel concentration (2.0–2.9) × 10^{-4} mol kg^{-1}; initial aluminium concentration (44.4–118.7) × 10^{-4} mol kg^{-1}. The points ▲, ✱ represent two independent experiments with a [Ni(sacsac)(PBu_3)Cl] precursor, the points ◆, ■, and × represent three independent experiments with a [Ni(sacsac)(PBu_3)Br] precursor



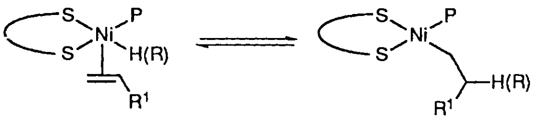
I



II

the catalytic cycle; and may be formed in the following series of steps.

The alkylated complex **II** may now form the hydride **I** by β elimination or it may react with incoming olefin substrate. Reaction with olefin substrate may occur *via* a five-co-ordinate intermediate or it may proceed without prior co-ordination of the olefin [equation (6)].



(6)

The observation that both R and L affect catalyst activity whilst only L affects the product distribution may be explained in terms of electronic and steric influences. It has been proposed that the major influence on product distributions in other catalyst systems is a steric one.[2] In the present systems the R groups on the backbone of the dithio-β-diketonate ligands are too far removed from the nickel centre to exert a significant steric effect. This is supported by the fact that *tert*-butyl groups in both the R^1 and R^3 positions of the dithio-β-diketonate ligand, within experimental error, do not change the product distributions with propylene substrate. However, changes in R are readily transmitted to the nickel centre *via* the delocalised electron system of the dithio-β-diketonate ligand. This influence is clearly demonstrated by inclusion of a CF_3 moiety on the sacsac backbone, leading to a large increase in catalyst activity.

It is, however, also possible that the activation process is an equilibrium involving dissociation of the dithiochelate and that this equilibrium is influenced by the electronic properties of the sulfur ligand. Changes in L on the phosphine ligand may influence the nickel centre both sterically and electronically.

Conclusion

The compounds [Ni{$R^1C(S)CR^2C(S)R^3$}($PL^1L^2L^3$)Cl] **2** are conveniently prepared from the corresponding bis(dithio-β-diketonato)nickel in high yield. Substituents R can readily be introduced at all positions around the dithio-β-diketonate ligand and can be used to modify the catalytic behaviour of catalysts derived from these compounds. Similarly, independent catalyst control *via* the phosphine substituents L is possible. The compounds **2** are thus extremely flexible catalyst precursors, and a considerable degree of control over the catalytic behaviour is possible. Thus, for example, the catalytic activity, selectivity and solubility can all be varied independently by suitable choices of the substituents R and L. These compounds can be isolated as well characterised molecular species useful in the generation of catalysts in homogeneous solution, or can be covalently anchored to insoluble supports such as silica–alumina or cross-linked polystyrene to form precursors of heterogeneous catalysts. The presence of both the nickel- and aluminium-containing components is necessary for catalytic activity and, unlike the behaviour of the related bis(β-diketonato)nickel derivatives, active oligomerization catalysts are not generated from bis(dithio-β-diketonato)nickel complexes under the conditions of our experiments.

In homogeneous solution under the conditions described, the reaction of propylene with examples of the catalyst system is at least 98% selective for dimers. In many other systems reported in the literature, the dimerization of propylene generally produces 10% or more of higher oligomers. Parallel with the high dimer selectivity of the catalyst system is high activity and a relatively long lifetime. Several of the new catalyst systems are among the most active reported for olefin dimerization and generally have operating lifetimes (with no apparent loss of catalytic activity) of at least 6 h. These compounds form even more active double-bond shift olefin isomerization catalysts. Terminal olefins are very rapidly isomerized to their internal isomers. This high isomerization activity may account for the high dimer selectivity if the relatively bulky internal olefins are less readily oligomerized than are terminal olefins.

Experimental

All manipulations were carried out in carefully dried apparatus under an atmosphere of dry nitrogen or argon using standard vacuum manifold and Schlenk techniques.[32] Where necessary, manipulations were carried out under dry, oxygen-free argon. Solvents were of A.R. quality and were dried and freshly distilled under nitrogen before use. 1,2-Dimethoxyethane was dried over sodium hydride, filtered, vacuum distilled and stored under argon. Chemical reagents for syntheses were at least of L.R. quality and were used as received. Gas feeds were CP grade and were passed through 3 Å molecular sieves before reaction. Hex-1-ene (Aldrich, analysed as 97.8% hex-1-ene, 2.2% *cis*-hex-3-ene) was freshly distilled from sodium under nitrogen. Tritetradecylphosphine, trihexadecylphosphine and trioctylphosphine were prepared by the method of Franks *et al.*[33] Other phosphine ligands were purchased from Strem Chemicals and from Aldrich Chemicals and were used as received. Phosphinated silica–alumina was prepared from $(EtO)_3SiCH_2CH_2PPh_2$ (Petrach) and silica–alumina (Strem, surface area 300 m^2 g^{-1});[34] [$Ni(cod)_2$] and 3,5-dimethyl-1,2-dithiolylium halides were prepared by literature methods;[20,35] Na(acac) and *endo*- and *exo*-5-acetylnorborn-2-ene, were synthesised as described in the literature;[36,37] [$Ni(sacsac)_2$], [Ni{$Bu^tC(S)CHC(S)Bu^t$}$_2$], and the compounds [$Ni(PL^1L^2L^3)_2X_2$] and

$[NiCl_2\{Ph_2PCH_2CH_2Si(OEt)_3\}_2]$ were prepared by literature methods.[38–42] The NMR spectra were recorded on JEOL FX-100, Bruker AC200F, CXP200, WM400 and AM300 spectrometers. Spectra were recorded at room temperature unless otherwise noted. Proton and ^{13}C NMR spectra were referenced either to internal $SiMe_4$ or to residual solvent resonances; ^{31}P NMR spectra were referenced to external H_3PO_4. Mass spectra were recorded on a modified MS-9 spectrometer at 70 eV (*ca.* 1.12×10^{-17} J) or on a Hewlett-Packard 5800 GC–MS instrument. The compounds $AlEt_3$ and $AlEt_2Cl$ (Aldrich) were used as received and were transferred using gas-tight syringes (Young's, Acton).

Gas chromatographic analyses were performed on a Hewlett-Packard 5790A gas chromatograph with a Hewlett-Packard 3393A integrator with an SGE 25 m QC2/BP1 0.25 mm capillary column. Propylene dimers (including *cis* and *trans* isomers) were individually resolved with an oven temperature of 0 °C, an isothermal time of 6.5 min and a ramp rate of 16 °C min^{-1}. The C_6 olefin isomers were identified from their retention times by comparisons with authentic samples and by a GC–MS method described earlier.[43]

Syntheses of β*-Diketones.*—The 3-substituted pentane-2,4-dione ligand precursors were synthesised by stirring the appropriate alkyl bromide and Na(acac) in ethanol [3-allylpentane-2,4-dione, b.p. 74–78 °C (8 Torr)] or dry dimethyl sulfoxide [3-butylpentane-2,4-dione, b.p. 100 °C (22 Torr); 3-(but-1-enyl)pentane-2,4-dione, b.p. 70 °C (3 Torr)] overnight.[44,45] 3-Benzylpentane-2,4-dione [b.p. 106 °C (< 1 Torr)] was prepared as a 2:1 mixture of keto and enol tautomers by refluxing Na(acac) in benzyl chloride for 8 h.[46] Thus, for example, in the preparation of 3-hexadecylpentane-2,4-dione, Na(acac) (12.00 g, 98 mmol) and degassed hexadecyl bromide (30.5 g, 100 mmol) were stirred in dry, oxygen-free dimethyl sulfoxide (150 cm^3) under argon at room temperature for 3 d, stirred at 50–60 °C for 3 d and then stirred at room temperature for 1 month. Water (500 cm^3) was added to the mixture which was extracted with benzene (6 × 150 cm^3). The combined benzene extracts were washed with water, and the benzene removed *in vacuo* to yield a light brown, low-melting solid. The solid was applied molten to a silica (230–400 mesh) chromatography column (3.5 × 38 cm) in two portions, and eluted with 30% hexane in dichloromethane under gravity. Unreacted hexadecyl bromide (9.36 g) was eluted first, followed by an off-white waxy solid. The solid product was recrystallised by dissolving in warm hexane and cooling to − 15 °C. The white product was collected by filtration at 0 °C, and washed with cold hexane. Further product was recovered from the mother-liquors. Drying under high vacuum gave 3-hexadecylpentane-2,4-dione as fluffy needles (yield 71%, m.p., 49–50 °C), which were characterised by mass spectroscopy (molecular ion *m/z* 324) and NMR: ^1H, δ 0.880 (3 H, m), 1.250 (28 H, m), 1.830 (2 H, m), 2.150 (6 H, s) and 3.602 (0.8 H, t, ^1J 7.26 Hz); ^{13}C, δ 14.07, 22.66, 27.56, 28.32, 28.95, 29.29, 29.45, 29.64, 31.90, 69.07 and 204.5.

Asymmetric substitution at R^1 and R^3 was achieved *via* the method of Ponticello and Furman.[36] For example, octadecane-8,10-dione was prepared by the addition of degassed decan-2-one (12 cm^3, 62 mmol) and degassed ethyl actanoate (38 cm^3, 194 mmol) to a suspension of sodium hydride (141 mmol) in freshly distilled dry oxygen-free 1,2-dimethoxyethane (130 cm^3) at 0 °C, followed by refluxing under argon for $2\frac{1}{2}$ h, neutralisation in ice (50 cm^3) with concentrated HCl (50 cm^3), extraction with chloroform, drying and isolation by vacuum distillation [57%, b.p. 144–148 °C (1 Torr)]. All β-diketones were identified by their ^1H NMR spectra.

*Syntheses of Bis(dithio-*β*-diketonato)nickel*(II) *Compounds* **1**.—The compounds $[Ni\{R^1C(S)CR^2C(S)R^3\}_2]$ were prepared *via* the method of Barraclough *et al.*[38] or of Stewart[47] and characterised by elemental analyses (Table 1), NMR and by the mass spectroscopic molecular ion. Most derivatives were crystalline. Two typical preparations are those of $[Ni\{MeC(S)C(CH_2Ph)C(S)Me\}_2]$ and the norbornenyl derivative $[Ni\{MeC(S)CHC(S)C_7H_9\}_2]$, below.

Bis(3-benzylpentane-2,4-dithionato)nickel(II), $[Ni\{MeC(S)C(CH_2Ph)C(S)Me\}_2]$. Hydrogen chloride gas was passed through methanol–ethanol (3:1 v/v, 40 cm^3) at 0 °C for 10 min. Nickel carbonate (1.5 g, 12.5 mmol) was added to the stirred solution, then 3-benzylacetylacetone (8.75 cm^3, 48.5 mmol) was added and a vigorous stream of H_2S was bubbled through the stirred solution at 0 °C for 2 h. The solution became deep green and seemingly 'set' with solid. The solution was warmed to room temperature and left stirring for 15 h with a gentle stream of H_2S passing through it. The dark green solid was filtered off, washed with methanol, recrystallised from chloroform–methanol and dried at the pump to yield olive-green crystals (66%).

endo- *and* exo-*Bis*{*4-(norbornen-4-yl)butane-2,4-dithionato*}*nickel*(II), $[Ni\{MeC(S)CHC(S)C_7H_9]$. Hydrogen chloride gas was passed through stirred methanol–ethanol (3:1 v/v, 80 cm^3) at 0 °C for 10 min. The solution was warmed to room temperature and nickel carbonate (1.5 g, 12.5 mmol) was dissolved in the solution. After cooling to 0 °C, *endo*- and *exo*-5-acetoacetylnorborn-2-ene (7.9 cm^3, 8.51 g, 47.8 mmol) was added and a vigorous stream of H_2S bubbled through the stirred solution for 2 h at 0 °C. The solution became dark green and a dark green solid was deposited. The solution was warmed to room temperature and left stirring for 15 h with a gentle stream of H_2S passing through it. The supernatant was decanted from the solid, and the solid washed with methanol until the washings were very pale. The solid was recrystallised from dichloromethane–methanol to yield the product as a dark green crystalline solid which was isolated by filtration, washed with methanol and dried at the pump (yield 3 g, 50%).

The presence of long-chain alkyl substituents resulted in the formation of oils. The modified syntheses required in such cases are illustrated by the preparation of $[Ni\{C_{18}H_{17}C(S)CHC(S)C_7H_{15}\}_2]$. Typically, HCl gas was passed through methanol–ethanol (3:1 v/v, 40 cm^3) at 0 °C for 10 min. The solution was warmed to room temperature and nickel carbonate (1.1 g, 9.2 mmol) added. The stirred solution was cooled to 0 °C and octadecane-8,10-dione (5 g, 18 mmol) added dropwise. A vigorous stream of H_2S was passed through the solution at 0 °C for 2 h. The solution was warmed to room temperature and a slow stream of H_2S passed through it for 15 h. A red-purple oil had separated from the light green alcoholic supernatant. The oil was isolated, washed several times with methanol, and extracted into diethyl ether. The solution was filtered and the oil precipitated with methanol. The product was separated by chromatography on silica gel with pentane as eluent to give a red-purple oil (yield 61%) at room temperature which can be recrystallised with care at low temperatures from chloroform and methanol. The oil was characterised by its mass spectrometry molecular ion (*m/z* 684).

(*Dithio-*β*-diketonato*)*halogeno*(*phosphine*)*nickel*(II) *Compounds* **2**.—*Method A*. The compounds $[Ni\{MeC(S)C(CH_2CH{=}CH_2)C(S)Me\}(PEt_3)Cl]$, $[Ni\{MeC(S)C(CH_2CH{=}CH_2)C(S)Me\}(PBu_3)Cl]$, $[Ni(sacsac)(PMe_3)Cl]$, $[Ni(sacsac)\{P(C_6H_{11})_3\}Cl]$, $[Ni\{MeC(S)C(CH_2Ph)C(S)Me\}(PBu_3)Cl]$, $[Ni\{MeC(S)CHC(S)C_7H_9\}(PBu_3)Cl]$, $[Ni\{Bu^tC(S)CHC(S)Bu^t\}(PBu_3)Cl]$, $[Ni\{MeC(S)CHC(S)CF_3\}(PEt_3)Cl]$, $[Ni(sacsac)(PPh_3)Cl]$, $[Ni(sacsac)(PPrPh_2)Cl]$, $[Ni\{MeC(S)CHC(S)CF_3\}(PBu_3)Cl]$, $[Ni(sacsac)\{P(C_8H_{17})_3\}Cl]$, $[Ni(sacsac)\{P(C_{14}H_{29})_3\}Cl]$, $[Ni(sacsac)\{P(C_{16}H_{33})_3\}Cl]$, $[Ni(sacsac)(PPhMe_2)Cl]$, $[Ni(sacsac)\{P(OEt)Ph_2\}Cl]$, $[Ni(sacsac)(PMePh_2)Cl]$ and $[Ni(sacsac)\{Ph_2PCH_2CH_2Si(OEt)_3\}Cl]$ were prepared by refluxing equimolar amounts of $[Ni\{R^1C(S)CR^2C(S)R^3\}_2]$ and $[Ni(PL_3)_2Cl_2]$ in benzene under an inert atmosphere.[11] The compounds were identified by a combination of elemental analyses, NMR spectroscopy and mass spectrometry.

Method B. The compounds [Ni(sacsac)(PEt$_3$)I], [Ni(sacsac)(PPh$_3$)I] and [Ni(sacsac){P(C$_6$H$_{11}$)$_3$}I] were prepared by oxidative addition of the 3,5-ditholylium cation to [Ni(cod)$_2$] in the presence of the appropriate phosphine. Typically, bis(1,5-cyclooctadiene)nickel(0) (0.72 g, 2.6 mmol) was dissolved in freshly distilled benzene (80 cm^3) under an argon atmosphere and the solution was cooled to 0 °C. Triethylphosphine (0.45 cm^3, 3 mmol) was added dropwise to the stirred solution and the resulting deep red mixture was treated with 3,5-dimethyl-1,2-ditholylium iodide (1.0 g, 3.8 mmol). Stirring was continued at room temperature for 24 h and the dark solid which precipitated from the deep red–purple solution was filtered off, dried and recrystallised from acetone–heptane (1:1) (20 °C) to give [Ni(sacsac)$_2$] as dark red-brown crystals (0.15 g, 18%) which were characterised by infrared and ^{1}H NMR spectroscopies. The filtrate was evaporated to dryness to obtain a dark red-purple solid which was recrystallised from dichloromethane–heptane (2:1) (−20 °C) to give [Ni(sacsac)(PEt$_3$)I] as dark crystals (0.55 g, 50%), m.p. 124 °C (decomp.). NMR: ^{1}H (CDCl$_3$, probe temperature 20 °C), δ 1.25 (dt, 9 H), 2.05 (dqnt, 6 H) and 7.30 (s, 1 H); ^{31}P (CD$_2$Cl$_2$), δ 18.38(s). IR (KBr): ν_{max} 2960, 2920, 2870, 1485, 1450, 1410, 1365, 1350, 1295, 1250, 1150, 1040, 1015, 835, 760, 740, 720, 630, 555 and 410 cm^{-1}.

Phosphinated Polystyrene.—Highly cross-linked (>50%) Amberlite XAD-4 polystyrene beads (20–60 mesh, 725 m^2 g^{-1} surface area) were thoroughly washed [25] and the resin was filtered off and dried *in vacuo* at 25 °C. A portion of the dried beads (20 g) was suspended in CCl$_4$ (300 cm^3) and brominated.[48–50] The straw coloured brominated beads were dried *in vacuo* at room temperature for 24 h ready for further treatment. Microanalysis indicated that the beads contained 22.8% (w/w) bromine, *i.e.*, approximately 40% of the polystyrene rings were brominated. Brominated beads (4.5 g) were then phosphinated by reaction with LiPPh$_2$.[50] The white to pale yellow phosphinated beads were thoroughly dried under vacuum and stored under argon.

Silica–Alumina-supported Nickel Dithioketonato Complexes.—Method A. Phosphinated silica–alumina support (1 g, 0.43 wt.% phosphorus) was loaded into a Schlenk tube under argon and [Ni(sacsac)(PPh$_3$)Cl] (0.105 g, 0.230 mmol) was loaded into a second tube under argon and dissolved in dry, degassed toluene (20 cm^3). This solution was added in small aliquots (about 2 or 3 cm^3) to the support with constant stirring. The colour of the solution over the support was allowed to fade before the next aliquot was added. The support was then stirred for 2 h in the presence of excess of complex. The excess of nickel complex and solvent were removed by decantation and the support washed with toluene (20 × 10 cm^3) by decantation. The final washings were colourless and the support was then a deep red-purple in colour. The support and complex were then dried under vacuum (10^{-3} Torr) at 50 °C for 3 h.

Method B. The complex [Ni(sacsac){Ph$_2$PCH$_2$CH$_2$Si(OEt)$_3$}Cl] was treated with silica–alumina (dried by heating at 250–300 °C under a vacuum of 10^{-3} Torr for 2 h) in refluxing benzene or toluene. The deep purple solid that was obtained was filtered off and washed with fresh solvent (benzene or toluene) and then extracted in a continuous extraction apparatus with refluxing solvent. The resulting solid was then dried under vacuum (10^{-3} Torr) for 3 h at 50 °C. Microanalysis of the resultant products showed that the loadings were close to those expected, and Ni:P:S ratios were generally within 5–10% of that required for supported complexes.

Polystyrene-supported [Ni(sacsac)(PPh$_3$)Cl].—Phosphinated beads (*ca.* 1–2 g) were loaded in a Schlenk tube, under argon and slurried with dry, degassed thf (*ca.* 5 cm^3). The complex [Ni(sacsac)(PPh$_3$)Cl] was loaded into a second Schlenk tube under argon and then dissolved in pure thf (*ca.* 10 cm^3). This solution was then added in small aliquots to the phosphinated resin and the mixture stirred after each addition until the supernatant was colourless. The supernatant was decanted from the resin after each aliquot to remove displaced, free PPh$_3$, thus reducing the likelihood of the back exchange reaction occurring. This procedure was continued until all the nickel complex had been loaded onto the beads or until the uptake of [Ni(sacsac)(PPh$_3$)Cl] ceased. The beads were then thoroughly washed with thf (5 × 10 cm^3) and dried *in vacuo* for 12 h at room temperature to give deep red-purple beads. In one example where an excess of phosphinated beads was used, NMR analysis of the residue from the combined decanted solvent fractions and washings indicated only free PPh$_3$. Approximately 80% of the expected PPh$_3$ was recovered. Samples with nickel contents of 0.19 and 0.47% (w/w) were prepared.

Catalytic Experiments.—Catalysts were tested as described previously [14,28] and by the following methods. Two methods of catalytic testing were employed in this work and are described below. The apparatus employed in catalytic testing depended on the test method used. In method 1 the apparatus consisted of a 500 cm^3 three-necked round-bottom Schlenk flask fitted with a gas bubbler and a rubber septum; the third neck was stoppered. In method 2 the apparatus consisted of a jacketed, 500 cm^3 three-necked round-bottom Schlenk flask, fitted with a gas inlet and a rubber septum. The Schlenk flask could be stirred magnetically or mechanically (preferred). Before proceeding with the experiments the apparatus was filled with purified argon.

Homogeneous Catalysts.—Method 1. Dry oxygen-free solvent (*ca.* 50 g) was transferred under argon into the reaction vessel. The vessel and contents were cooled in a bath maintained at −15 °C. Dry olefin was bubbled through the solution at a constant inlet flow rate (*e.g.*, with propylene, approximately 150 cm^3 min^{-1}). This gas flow was maintained throughout the duration of the experiment. Co-catalyst (AlEt$_2$Cl, approximately 0.1–0.15 cm^3) was added by syringe 20–30 min after the commencement of the passage of gas, to allow saturation of the solvent with gas. One hour after the addition of the co-catalyst an aliquot of the solution was taken for gas chromatographic analysis as a pre-run blank. After a further 10 min a solution of the nickel complex (approximately 2.50 × 10^{-5} mol in 5–10 g solvent) was transferred under argon to the mixture. Aliquots were taken from the reaction mixture at various periods during the experiment, deactivated by shaking with dilute aqueous hydrochloric acid, and then analysed by gas chromatography.

To establish what effect, if any, the co-catalyst (AlEt$_2$Cl) may have had on the dimerization of propylene, a blank experiment, *i.e.*, without the nickel complex, was carried out under the same conditions as those employed in the catalytic experiment above. No dimerization or oligomerization of propylene was detectable after 4 h of operation.

In the reaction with ethylene, the same procedure was followed with a gas flow rate of 250 cm^3 min^{-1}, toluene as solvent and AlEt$_2$Cl as the co-catalyst. On the gas outlet side of the apparatus, two cold traps (held at −68 °C) were fitted to trap out any volatile products carried through by unreacted ethylene.

Method 2. The second method employed the jacketed reaction vessel and was operated as a closed system. The feed gas cylinder (*ca.* 3 kg gross), which was placed on a top-loading balance, was connected to the reaction vessel *via* a constant 0.5–1 lbf in^{-2} pressure regulator. In this way, the reaction vessel was maintained under a low constant pressure of propylene. As the substrate was consumed more would flow to the reactor. Consumption with time was monitored with the balance. A full description of the apparatus and its mode of operation has been given previously.[21,28] Modifications to the apparatus described previously included the use of a high speed mechanical stirrer fitted with a stainless steel quickfit joint, a turbine type stirrer blade and a hollow stirrer shaft for the introduction of gas. This stirrer arrangement ensured rapid and efficient mixing. Catalytic testing was generally carried out at 0 ± 1 °C in chlorobenzene as solvent, however in several experiments pure hydrocarbon solvents were used. These were heptane and oct-1-ene.

Catalysts for propylene and ethylene oligomerization were tested for between 3 and 8 h (occasionally longer), and all experiments were repeated at least once.

Heterogeneous Olefin Oligomerization.—The same apparatus, conditions and procedures as employed for the homogeneous system were used. Propylene was the feed olefin, and toluene the solvent. However, approximately 60 min after the addition of co-catalyst and after the removal of the pre-run blank, the solid anchored catalyst precursor was added under pure, dry argon *via* a Schlenk-type solids transfer pistol (0.3 to 0.9 g of solid sample was added, depending on the percentage of nickel present) through the third neck of the reaction vessel. Thus a three phase system was obtained. Aliquots were taken at various intervals and analysed by gas chromatography.

Homogeneous Olefin Isomerization.—Hex-1-ene (5 g) was dissolved in pure, dry toluene (42 g) at −15 °C. Co-catalyst, $AlEt_2Cl$, was added and the solution stirred at −15 °C for 1 h. After this time an aliquot was withdrawn as a pre-run blank, and analysed by gas chromatography (no isomerization or oligomerization was detected). A toluene solution of [Ni(sacsac)-$(PBu_3)Cl$] (0.3104 g, 2.4315×10^{-5} mol in 5 g toluene) was then added and aliquots were periodically withdrawn, deactivated (with 0.1 mol dm^{-3} HCl) and analysed by gas chromatography. Only isomerization was observed. There was no detectable hexene oligomerization under the conditions of this experiment.

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