Syntheses and Structures of Nickel(0) Complexes containing the Methyl Methacrylate Monomer as Ligand †

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The reaction of [Ni(η^4-C_8H_{12})$_2$] with the industrially important monomer methyl methacrylate, CH_2=C(Me)CO_2Me, in the presence of 1 or 2 mol equivalents of tricyclohexylphosphine leads to the formation of [Ni{η^2-CH_2=C(Me)CO_2Me}{P(C_6H_{11})$_3$}$_2$] **1** and [Ni{η^2-CH_2=C(Me)CO_2Me}$_2${P(C_6H_{11})$_3$}] **2**, respectively. The crystal structures of **1** and **2** have been determined and reveal an η^2-CC mode of co-ordination of the methyl methacrylate ligands, with the CO_2Me groups pendant and outside the nickel co-ordination sphere. Complexes **1** and **2** represent the first structurally characterised methyl methacrylate complexes; **2** is formed as a mixture of *meso* and DL diastereomers in the ratio 2.34:1. Solution NMR studies indicate that the diastereomers interconvert rapidly, *via* an intramolecular mechanism, which is proposed to proceed *via* an O-co-ordinated intermediate. Reaction of **1** with an excess of *tert*-butyl acrylate CH_2=CHCO_2Bu^t yields [Ni(η^2-CH_2=CHCO_2Bu^t)$_2${P(C_6H_{11})$_3$}] **4**, which may be prepared independently from [Ni(η^4-C_8H_{12})$_2$], P(C_6H_{11})$_3$ and *tert*-butyl acrylate.

It has been known for over thirty years that certain nickel-containing compounds are active catalysts for a range of processes including the dimerisation of ethylene and the cyclooligomerisation of butadiene and alkynes.[1] Continuing interest in the application of organometallic complexes of nickel to alkene functionalisation is widespread. For example, in a mechanistic investigation, various nickel species have been identified, using extended X-ray absorption fine structure spectroscopy (EXAFS), in [Ni(acac)$_2$]–cyclooctadiene–AlEt$_3$ (Hacac = acetylacetone = pentane-2,4-dione) mixtures treated with allyl bromide and triphenylphosphine.[2] Such mixtures are well known to catalyse the dimerisation of ethylene. The activity of various well defined cationic methallyl nickel(II) complexes for ethylene oligomerisation has recently been described,[3] and in a related study [{Ni(η^3-C_3H_5)(OR)}$_2$] (R = a range of aryl groups) complexes have been used to initiate the polymerisation of 1,3-dienes to form high molecular weight 1,4-linked polymers.[4] Novak and co-workers[5] have used a dinuclear nickel complex for the living polymerisation of butadiene and various isocyanides, yielding block co-polymers containing linear blocks of non-polar polybutadiene and polar polyisocyanide. The polymerisation of the vinyl monomer methyl methacrylate, CH_2=C(Me)CO_2Me, using [NiCl$_2$(PPh$_3$)$_2$]–LiBu mixtures has been recently reported.[6] The role of the nickel in this reaction is unclear at the present time. Such late transition-metal systems are potentially more attractive than early transition-metal alkene polymerisation catalysts[7] because they are more resilient to the oxygen functionality present in the methyl methacrylate monomer, and polymerisation reactions can therefore be carried out at ambient temperatures or above. Under comparable conditions, many early transition-metal catalysts are deactivated very quickly. There is growing interest in the development of polymerisation catalysts which are stable towards a variety of functional groups (*e.g.* amido, –NR$_2$, ether or hydroxy, –OR, ester or carboxylic acid, CO_2R *etc.* where R is alkyl[8] or H[9]) and which can be used in the presence of environmentally acceptable protic solvents.[10] The acrylic family of monomers represent an industrially important set of polymer building blocks offering a range of properties with applications varying from aircraft windows to surface coatings and adhesives. A range of new polymerisation strategies have been developed over the last ten years in order to achieve controlled polymerisation of the vinyl double bond without reaction at the ester functional group.[11] However, the co-ordination chemistry of acrylic monomers is under-developed at the present time.

Given the proven ability of [Ni{P(C_6H_{11})$_3$}$_n$] (n = 1 or 2) fragments to form alkene and alkyne complexes of reasonable thermal stability,[12] and following on from related studies of Yamamoto and co-workers,[13] we have undertaken a study of the reaction of [Ni(η^4-C_8H_{12})$_2$] with acrylates (and, in particular, methyl methacrylate), in the presence of tricyclohexylphosphine. In this paper we describe the synthesis and properties of nickel complexes containing one or two co-ordinated methyl methacrylate units, and provide information on their spectroscopic properties and solid state structures. These compounds represent the first structurally characterised nickel(methyl methacrylate) complexes, and offer insight into the mechanism of reaction in nickel-based acrylic polymerisation systems.

Results and Discussion

Reaction of [Ni(η^4-C_8H_{12})$_2$] with 2 mol equivalents of tricyclohexylphosphine in the presence of an excess of methyl methacrylate yields, after purification, yellow crystals of [Ni{η^2-CH_2=C(Me)CO_2Me}{P(C_6H_{11})$_3$}$_2$] **1** in high yield, Scheme 1. While **1** is thermally stable (crystals may be stored at 5 °C over several months with no decomposition), it is air-sensitive as a solid and solutions decompose in seconds upon exposure to air. In this respect, **1** typifies the new nickel–methyl methacrylate complexes described in this paper. Analytical and spectroscopic data are summarised in Table 1. The low-temperature crystal structure has been determined, and shows that **1** crystallises in the monoclinic space group $P2_1/n$. The fractional atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3. The molecular structure of **1** is shown in Fig. 1. The nickel atom adopts a pseudo-trigonal geometry, as is commonly found for three-coordinate, 16-electron complexes of nickel(0).[14] The cyclohexyl rings all take

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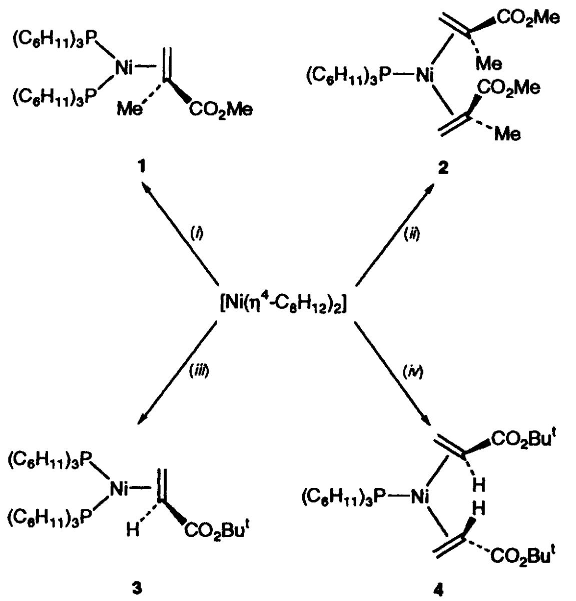
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical and spectroscopic data for complexes **1**, **2** and **4**

Complex	**1**	**2**[a]	**4**[b]
Analysis[c] (%) C	67.95 (68.50)	62.05 (62.35)	64.70 (64.60)
H	9.90 (10.40)	9.30 (9.15)	9.90 (9.70)
IR[d] (cm^{-1})	1678s	1703s, 1686s	1694s, 1681s
^{1}H NMR[e]	3.55 (3 H, s, OMe)	3.46 (3 H, s, OMe)	4.24 [1 H, ddd, *J*(HH) = 12.2, *J*(HP) = 8.8, *J*(HH) = 3.8, $=CH$]
	2.38 [1 H, ddd, *J*(HP) = 7.5, 6.5, *J*(HH) = 3.7, $=CH_2$]	3.29 [1 H, dd, *J*(HP) = 9.5, *J*(HH) = 1.5, $=CH_2$]	3.48 [1 H, dd, *J*(HH) = 12.2, *J*(HP) = 7.8, $=CH_2$]
	2.09–0.84 (m, C_6H_{11})	2.63 [1 H, dd, *J*(HP) = 6.5, *J*(HH) = 1.5, $=CH_2$]	2.83 [1 H, dd, *J*(HP) = 8.4, *J*(HH) = 3.8, $=CH_2$]
	1.97 (3 H, Me)[f]	2.05–1.05 (m, C_6H_{11})	2.08–1.00 (m, C_6H_{11})
	1.96 (1 H, $=CH_2$)[f]	1.75 [3 H, d, *J*(HP) = 4.0, Me]	1.56 (9 H, s, CMe_3)
^{31}P NMR	37.1 [d, *J*(PP′) = 32.5]	38.2	39.4
	31.1 [d, *J*(PP′) = 32.5]		
^{13}C NMR[g]	176.2 (CO_2)	173.2 (CO_2)	171.3 [d, *J*(PC) = 2.7, CO_2]
	49.9 (OMe)	67.6 [d, *J*(PC) = 8.3, $=C$]	78.3 (*C*Me_3)
	48.4 [dd, *J*(PC) = 3.2, 2.4, $=C$]	59.0 ($=CH_2$)	63.4 [d, *J*(PC) = 6.6, $=CH$]
	42.6 [dd, *J*(PC) = 6.4, 5.6, $=CH_2$]	50.5 (OMe)	53.3 [d, *J*(PC) = 6.2, $=CH_2$]
	37.8 [d, *J*(PC) = 11.9, CH of C_6H_{11}]	35.8 [d, *J*(PC) = 16.5, CH of C_6H_{11}]	36.1 [d, *J*(PC) = 17.6, CH of C_6H_{11}]
	36.8 [d, *J*(PC) = 12.1, CH of C_6H_{11}]	30.6 (CH_2 of C_6H_{11})	30.8 (CH_2 of C_6H_{11})
	31.2 (CH_2 of C_6H_{11})[h]	28.2(CH_2 of C_6H_{11})	30.6 (CH_2 of C_6H_{11})
	28.4 (CH_2 of C_6H_{11})[h]	27.1 (CH_2 of C_6H_{11})	28.6 (CMe)$_3$
	27.2 (CH_2 of C_6H_{11})[h]	18.1 (Me)	28.1 (CH_2 of C_6H_{11})
	22.0 (Me)		26.9 (CH_2 of C_6H_{11})

[a] Data for *meso* diastereomer given. Data for DL isomer is as follows. ^{1}H NMR: δ 3.65 (OMe), 3.31 [dd, *J*(HP) = 7.6, *J*(HH) = 1.5, $=CH_2$], 2.61 [dd, *J*(HP) = 7.9, *J*(HH) = 1.5, $=CH_2$] and 1.76 [d, *J*(HP) = 4.6, Me], cyclohexyl resonances overlap with those of **2** (*meso*); ^{31}P NMR: δ 37.7; ^{13}C NMR: δ 173.1 (CO_2), 67.74 [d, *J*(PC) = 8.5, $=C$], 59.06 ($=CH_2$), 50.64 (OMe) and 19.40 (Me). [b] Data for DL diastereomer given. [c] Analytical data given as found (required). [d] Nujol mull. [e] In C_7D_8 solution (295 K), data given as: chemical shift (δ) (relative intensity, multiplicity, *J*/Hz, assignment). [f] Resonances obscured by broad complex resonances due to cyclohexyl groups; located using nuclear Overhäuser effect (NOE) and ^{13}C–^{1}H correlation spectroscopy. [g] Assignments assisted by distortionless enhancements by polarisation transfer (DEPT) and ^{13}C–^{1}H correlation spectroscopy. [h] Cyclohexyl CH_2 groups show extra resonances due to hindered rotation about the Ni–P bonds. Peaks for principal rotamers given.

up the chair conformation, and the two $P(C_6H_{11})_3$ ligands have their rings staggered with respect to one another. The Ni–P bond lengths of 2.211(3) and 2.222(3) Å are within two standard deviations of each other, and so are not significantly different. They are comparable to other complexes containing the $Ni\{P(C_6H_{11})_3\}_2$ fragment, see Table 4. The P–Ni–P angle of 118.5°, while large for bis(phosphine) nickel complexes[15] is similar to related complexes, as shown in Table 4, and reflects the very large steric demands of three cyclohexyl groups. The Ni–C(2) bond length of 2.023(11) Å is considerably longer than the Ni–C(1) bond length [1.975(10) Å], as expected for a geminally disubstituted alkene ligand. The lengthening of the C(1)–C(2) bond to 1.410(13) Å as compared with 1.331 Å in diphenylmethyl methacrylate[16] shows a significant degree of back bonding between the electron-rich nickel and the alkene moiety, due to the presence of the basic $P(C_6H_{11})_3$ ligands. The Me and CO_2Me substituents are bent away from the nickel centre, such that the C(3)–C(2)–C(4) angle is compressed to 112.7(10)°. The very short C(3)–O(1) bond length of 1.236(12) Å is indicative of a localised C=O group, in which the π system is isolated from the conjugated C(1)–C(2) π bond. The O atoms are 3.79 [O(1)] and 3.10 Å [O(2)] from the nickel; these distances are longer than the Ni • • • C(4) distance of 3.08 Å and indicate that the oxygen atoms are not involved in the bonding to the nickel at all. The observation of an intense band at 1678 cm^{-1} in the IR spectrum, assigned to the ν(CO) stretching mode, supports this. The bonding of the methyl methacrylate in **1** is thus classified as η^2-CC. The C(1) and C(2) atoms lie very close to the plane defined by the nickel and two phosphorus atoms; the Ni–C(1)–C(2) plane is tilted by only 1.6° from the Ni–P(1)–P(2) plane.



Scheme 1 Synthesis of complexes **1**–**4**. (*i*) 1 : 2 Ni : $P(C_6H_{11})_3$ mole ratio, excess of methyl methacrylate, 0 °C; (*ii*) 1 : 1 mole ratio, excess of methyl methacrylate, 0 °C; (*iii*) 1 : 1 mole ratio, excess of *tert*-butyl acrylate, 0 °C; (*iv*) $P(C_6H_{11})_3$, 1 mol equivalent *tert*-butyl acrylate, 0 °C

The ^{31}P NMR spectrum of **1** in toluene solution at room temperature shows a pair of doublets at δ 37.1 and 31.1 [$J(PP')$ = 32.5 Hz]. The inequivalent phosphorus atoms indicate that the co-ordinated methyl methacrylate rotates, at most, very slowly on the NMR time-scale. Warming the solution to 358 K (at which point, the compound begins to decompose) does not significantly alter the appearance of the spectrum.

The identification of **1** as an η^2-CC bonded complex of type **A** is unsurprising; the late, carbophilic nickel(0) centre might be expected to bond preferentially through the olefinic double bond.

Table 3 Selected bond lengths (Å) and angles (°) for complex **1**

Ni–C(1)	1.975(10)	C(2)–C(4)	1.507(14)
Ni–C(2)	2.023(11)	O(1)–C(3)	1.236(12)
C(1)–C(2)	1.410(13)	O(2)–C(3)	1.365(12)
C(2)–C(3)	1.419(14)	O(2)–C(5)	1.422(11)
C(1)–Ni–C(2)	41.3(4)	C(1)–C(2)–C(4)	119.9(10)
C(1)–Ni–P(1)	92.1(3)	C(3)–C(2)–C(4)	112.7(10)
C(2)–Ni–P(1)	133.3(3)	C(1)–C(2)–Ni	67.5(6)
C(1)–Ni–P(2)	149.4(3)	C(3)–C(2)–Ni	108.7(8)
C(2)–Ni–P(2)	108.1(3)	C(4)–C(2)–Ni	119.9(8)
P(1)–Ni–P(2)	118.50(13)	O(1)–C(3)–O(2)	120.0(11)
C(3)–O(2)–C(5)	115.3(9)	O(1)–C(3)–C(2)	127.2(12)
C(2)–C(1)–Ni	71.2(6)	O(2)–C(3)–C(2)	112.8(10)
C(1)–C(2)–C(3)	120.2(11)		

Table 2 Fractional atomic coordinates (× 10^4) for complex **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni	1 406.1(12)	9 180.8(6)	7 201.9(10)
P(1)	638(2)	8 578.4(12)	6 151(2)
P(2)	2 153(2)	8 862.8(12)	8 596(2)
O(2)	3 372(6)	9 924(3)	6 522(5)
O(1)	3 362(7)	10 400(3)	7 898(6)
C(1)	1 088(10)	9 811(4)	6 322(8)
C(2)	1 624(9)	10 015(4)	7 184(8)
C(3)	2 820(10)	10 134(4)	7 262(9)
C(4)	960(9)	10 379(5)	7 817(8)
C(5)	4 561(9)	10 057(5)	6 532(8)
C(100)	368(10)	7 816(4)	6 273(9)
C(101)	1 372(10)	7 451(5)	6 329(10)
C(102)	1 098(10)	6 838(4)	6 365(9)
C(103)	315(11)	6 709(5)	7 122(9)
C(104)	−709(11)	7 059(5)	7 041(10)
C(105)	−426(9)	7 676(4)	7 028(7)
C(110)	1 445(8)	8 552(4)	5 059(7)
C(111)	2 735(8)	8 616(5)	5 327(8)
C(112)	3 434(9)	8 553(5)	4 466(8)
C(113)	3 043(9)	8 968(5)	3 710(8)
C(114)	1 791(9)	8 894(5)	3 429(8)
C(115)	1 064(9)	8 952(4)	4 246(7)
C(120)	−807(8)	8 831(4)	5 708(7)
C(121)	−1 513(9)	9 057(4)	6 490(7)
C(122)	−2 545(9)	9 345(4)	6 046(7)
C(123)	−3 282(9)	8 991(5)	5 385(8)
C(124)	−2 600(9)	8 758(4)	4 604(7)
C(125)	−1 534(8)	8 450(4)	5 030(7)
C(200)	2 563(8)	9 419(4)	9 503(7)
C(201)	3 547(8)	9 296(4)	10 258(7)
C(202)	3 847(9)	9 820(5)	10 843(8)
C(203)	2 829(10)	10 037(5)	11 302(8)
C(204)	1 866(9)	10 160(4)	10 558(8)
C(205)	1 543(8)	9 642(4)	9 995(7)
C(210)	1 246(8)	8 356(4)	9 167(7)
C(211)	1 692(9)	8 142(5)	10 157(7)
C(212)	913(10)	7 693(5)	10 494(8)
C(213)	−302(11)	7 886(5)	10 520(8)
C(214)	−774(10)	8 095(5)	9 535(8)
C(215)	2(8)	8 546(4)	9 183(7)
C(220)	3 513(9)	8 496(4)	8 538(9)
C(221)	3 565(10)	7 944(5)	8 195(10)
C(222)	4 732(8)	7 674(4)	8 218(8)
C(223)	5 609(11)	8 037(5)	7 826(10)
C(224)	5 580(11)	8 600(6)	8 148(11)
C(225)	4 408(8)	8 866(4)	8 099(7)

Table 4 Comparison of Ni–P bond lengths and P–Ni–P angles in selected complexes containing the $Ni\{P(C_6H_{11})_3\}_n$ (n = 1 or 2) fragment

Complex	Ni–P/Å[a]	P–Ni–P/°	Ref.
$[Ni\{P(C_6H_{11})_3\}_2(\eta^2\text{-}MeOCH_2C{\equiv}CCH_2OMe)]$	2.20	115.1	14*a*
$[Ni\{P(C_6H_{11})_3\}_2(\eta^2\text{-}C_{14}H_{10})]$[b]	2.23	118.3	14*b*
1	2.217(3)	118.5	This work
$[Ni\{P(C_6H_{11})_3\}_2(\eta^1\text{-}SO_2)]$	2.21	118.9	14*c*
$[Ni\{P(C_6H_{11})_3\}_2(\eta^2\text{-}PhCHO)]$	2.17, 2.24	118.9	14*d*
$[Ni\{P(C_6H_{11})_3\}_2(\eta^2\text{-}CO_2)]$	2.16, 2.29	122.6	14*e*
$[\{Ni[P(C_6H_{11})_3]_2\}_2(\mu_2\text{-}N_2)]$	2.18	128.0, 129.3	14*f*
$[Ni\{P(C_6H_{11})_3\}(\eta^2\text{-}C_2H_4)_2]$	2.20		14*g*
2	2.215(3)		This work

[a] Given as average where the two bond lengths are not significantly different. All bond lengths quoted have estimated standard deviations of 0.01 Å or smaller. [b] $C_{14}H_{10}$ = anthracene.

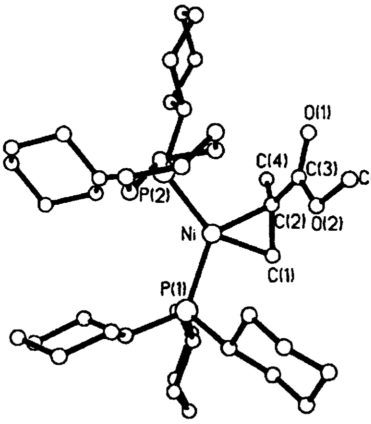
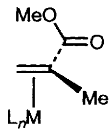


Fig. 1 Molecular structure of $[Ni\{\eta^2\text{-}CH_2{=}C(Me)CO_2Me\}\{P(C_6H_{11})_3\}_2]$ **1**



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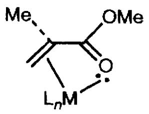

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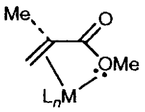

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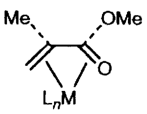
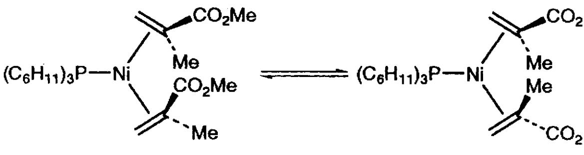


D

However, acrylics may, in principle, bond in several ways to transition-metal centres, as exemplified by structures **B** to **D**. Recent EXAFS and IR data indicate that $TiCl_4$ co-ordinates up to two methyl acrylate ligands in dichloromethane solution.[17] The acrylate ligands are believed to bond to the hard, oxophilic titanium centre through the carbonyl oxygen atoms. A similar mode of binding through an ester carbonyl group has been structurally characterised in $[TiCl_4\{EtOC(O)C_6H_4OMe\text{-}p\}]$.[18] In an effort to identify such a chelating mode of co-ordination of methyl methacrylate to nickel, experiments were undertaken where the relative amount of phosphine donor ligand was cut or removed completely. Reaction of $[Ni(\eta^4\text{-}C_8H_{12})_2]$ with 1 mol equivalent of tricyclohexylphosphine in the presence of a large excess of methyl methacrylate leads to the formation of $[Ni\{\eta^2\text{-}CH_2{=}C(Me)CO_2Me\}_2\{P(C_6H_{11})_3\}]$ **2** in high yield. The low-temperature crystal structure has been determined, and shows **2** to crystallise in the triclinic space group $P\bar{1}$. The fractional atomic coordinates are given in Table 5 and selected bond lengths and angles in Table 6. The molecular structure of **2** is shown in Fig. 2. As in **1**, the complex has pseudo-trigonal geometry. The Ni–P bond length (Table 4) of 2.215(3) Å is essentially identical to the comparable bonds in **1** and in $[Ni(C_2H_4)_2\{P(C_6H_{11})_3\}]$,[14g] and again, the cyclohexyl rings are bound equatorially to the phosphorus. The geometries of the two methyl methacrylate ligands are not significantly different, within the precision of the bond lengths. The angle subtended at the nickel by the centres of the double bonds is 135.2°, which is somewhat larger than that in $[Ni(C_2H_4)_2\{P(C_6H_{11})_3\}]$ of 126.9°. The methyl methacrylate ligands are bound 'head-to-head', that is with the Me and CO_2Me substituents close together. This is presumably due to the steric demands of the $P(C_6H_{11})$ ligand, which occupies nearly one face of the metal [the cone angle of $P(C_6H_{11})_3$ is 170°].[19] There is a distinct twist in the relative orientations of the methyl methacrylate ligands; the Ni–C(1)–C(2) plane is tilted at 25.4° to the Ni–C(6)–C(7) plane. This allows the Me and CO_2Me groups to adopt a staggered conformation, and thereby minimises steric interactions between the methacrylate ligands. As described for **1**, the O atoms are all at least 2.95 Å away from the nickel atom. This is comparable to, or longer than, the separation between the nickel and C(3)/C(8) methyl carbon atoms, indicating that there are no significant Ni–O interactions. The bonding of both methyl methacrylate ligands in **2** is best described as η^2-CC. As in **1**, this is supported by the observation of two intense ν(CO) bands at 1686 and 1703 cm^{-1} in the IR spectrum. Thus, a chelating mode of co-ordination of methyl methacrylate is not favoured, at least under the conditions of our experiment where methyl methacrylate is always present in excess (we have observed that solutions of **1** and **2** are noticeably less stable in the absence of free methyl methacrylate).

The ^{31}P NMR spectrum of **2** in toluene solution at room temperature consists of two singlets at δ 38.2 and 37.7, in the relative ratio 2.34 : 1. We presume the major isomer to have a structure close to the solid-state structure of **2**. The absence of free methyl methacrylate and tricyclohexylphosphine in solution argues against the possibility of the minor product being formed by decomposition. We ascribe the two peaks to the presence of diastereomers in solution, equation (1), where **E**, the major *meso* component, is the solid-state structure and **F** the other pair of DL diastereomers (the chirality in **2** arises through the co-ordination of the geminally disubstituted alkene to the metal centre).



E(*meso*-**2**) **F**(DL-**2**)

(1)

The possibility that the minor isomer is due to a 'head-to-tail' rotamer is discounted because such a complex requires resonances in the ^1H and ^{13}C NMR spectra for two inequivalent methyl methacrylate ligands. This is not observed; the isomers each contain identical pairs of methacrylate ligands. This is expected for **E** and **F** which have a mirror plane and a C_2 axis symmetry element present, respectively. Spin-saturation transfer experiments conducted at room temperature indicate that interconversion between isomers is relatively rapid (of the order of seconds). Gradual warming of the solution to 333 K causes broadening and eventual coalescence of the signals. However, **2** decomposes quickly at these elevated temperatures, and a more detailed analysis has not been undertaken.

Table 5 Fractional atomic coordinates (× 10^4) for complex **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni	3595.6(7)	4863.9(6)	7031.9(6)
P	2572.1(14)	2994.3(11)	6404.8(12)
O(1)	3079(4)	8150(3)	8215(4)
O(2)	1952(4)	6517(3)	8103(3)
O(3)	5336(4)	7205(3)	9838(3)
O(4)	6398(4)	7818(3)	8902(3)
C(1)	1903(6)	5120(5)	5860(5)
C(2)	2843(5)	6225(4)	6623(5)
C(3)	3590(6)	6793(5)	6132(5)
C(4)	2667(6)	7071(5)	7714(5)
C(5)	1912(7)	7269(6)	9255(5)
C(6)	5315(6)	4783(5)	8318(5)
C(7)	5636(5)	5752(4)	8113(4)
C(8)	6441(6)	5605(5)	7333(5)
C(9)	5741(5)	6975(5)	9044(5)
C(10)	6537(6)	9053(4)	9752(5)
C(11)	1239(5)	2905(4)	6988(4)
C(12)	1900(5)	3629(5)	8393(4)
C(13)	878(6)	3442(5)	8927(5)
C(14)	−531(6)	3748(5)	8339(5)
C(15)	−1169(6)	3042(6)	6952(5)
C(16)	−160(5)	3277(5)	6441(5)
C(21)	1569(5)	2193(4)	4715(4)
C(22)	816(5)	878(4)	4144(5)
C(23)	−132(6)	439(5)	2776(5)
C(24)	693(6)	586(5)	2091(5)
C(25)	1477(6)	1880(5)	2660(5)
C(26)	2437(5)	2319(5)	4022(4)
C(31)	3747(5)	2025(4)	6922(5)
C(32)	3097(5)	911(5)	6925(5)
C(33)	4246(5)	337(4)	7529(5)
C(34)	5245(6)	3(5)	6908(5)
C(35)	5890(5)	1110(5)	6889(5)
C(36)	4737(5)	1683(4)	6283(5)

Table 6 Selected bond lengths (Å) and angles (°) for complex **2**

Ni–C(1)	1.981(6)	Ni–C(6)	1.979(6)
Ni–C(2)	2.044(5)	Ni–C(7)	2.036(6)
C(1)–C(2)	1.397(7)	C(6)–C(7)	1.391(7)
C(2)–C(3)	1.497(7)	C(7)–C(8)	1.511(7)
C(2)–C(4)	1.472(7)	C(7)–C(9)	1.482(7)
O(1)–C(4)	1.209(6)	O(3)–C(9)	1.198(6)
O(2)–C(4)	1.357(6)	O(4)–C(9)	1.353(6)
O(2)–C(5)	1.435(7)	O(4)–C(10)	1.447(6)
C(1)–Ni–C(2)	40.6(2)	C(4)–O(2)–C(5)	115.2(5)
C(1)–Ni–C(6)	174.2(2)	C(4)–C(2)–C(3)	115.1(5)
C(1)–Ni–C(7)	135.7(2)	C(4)–C(2)–Ni	105.4(3)
C(2)–Ni–C(6)	134.1(2)	O(1)–C(4)–O(2)	122.2(5)
C(2)–Ni–C(7)	96.7(2)	O(1)–C(4)–C(2)	125.0(6)
C(6)–Ni–C(7)	40.5(2)	O(2)–C(4)–C(2)	112.8(5)
C(1)–Ni–P	91.7(2)	C(6)–C(7)–C(8)	118.8(5)
C(2)–Ni–P	131.8(2)	C(6)–C(7)–C(9)	117.3(5)
C(6)–Ni–P	93.2(2)	C(6)–C(7)–Ni	67.5(3)
C(7)–Ni–P	131.4(2)	C(7)–C(6)–Ni	72.0(3)
C(11)–P–Ni	113.4(2)	C(8)–C(7)–Ni	110.2(3)
C(21)–P–Ni	112.5(2)	C(8)–C(7)–C(9)	118.8(5)
C(31)–P–Ni	116.2(2)	C(9)–C(7)–Ni	112.1(4)
C(1)–C(2)–C(3)	120.9(5)	C(9)–O(4)–C(10)	115.3(4)
C(1)–C(2)–C(4)	119.1(5)	O(3)–C(9)–O(4)	123.7(5)
C(1)–C(2)–Ni	67.3(3)	O(3)–C(9)–C(7)	125.8(5)
C(3)–C(2)–Ni	118.5(4)	O(4)–C(9)–C(7)	110.5(5)

It is not possible to interconvert **E** and **F** by a simple rotation. The mechanism of interchange must occur either (*a*) by ligand dissociation of one methyl methacrylate leading to a co-ordinatively unsaturated intermediate possibly of type **B**, followed by reco-ordination (an intermolecular rearrangement), or (*b*) *via* an intermediate similar to **B** (or **C**), in which O-atom co-ordination precedes dissociation of the C–C double bond (an intramolecular rearrangement), as shown in Scheme 2. In order to distinguish between these mechanisms, a separate NMR experiment in which **2** and methyl methacrylate were dissolved in [$^2H_8$]toluene was conducted. The appearance of the resonances of **2** is unaffected by the presence of free methyl methacrylate, and there is no spin-saturation transfer between free and bound methacrylate units. This argues against the intermolecular mechanism (*i*) and in favour of an intramolecular mechanism such as (*ii*).

In preliminary studies, the reactivity of **1** towards mono- and tri-substituted alkenes has been investigated, Scheme 3. Reaction with excess *tert*-butyl acrylate leads to [Ni(η^2-CH$_2$=CHCO$_2$Bu^t)$_2${P(C$_6$H$_{11}$)$_3$}] **4**, with both methyl methacrylate and tricyclohexylphosphine ligands substituted. Reaction occurs within minutes at room temperature. Compound **4** and [Ni(CH$_2$=CHCO$_2$Bu^t){P(C$_6$H$_{11}$)$_3$}$_2$] **3** have been synthe-

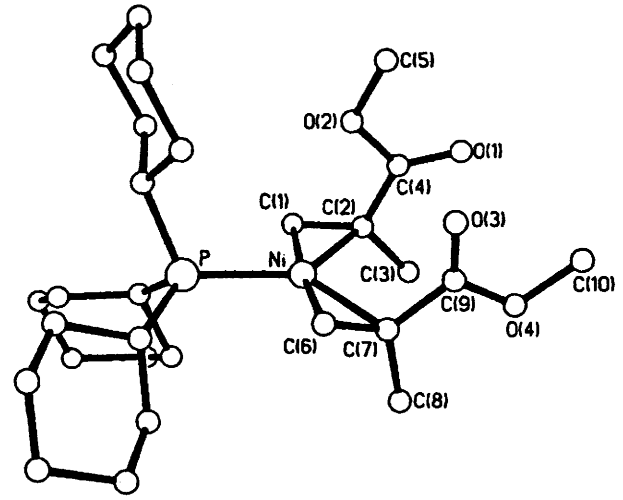
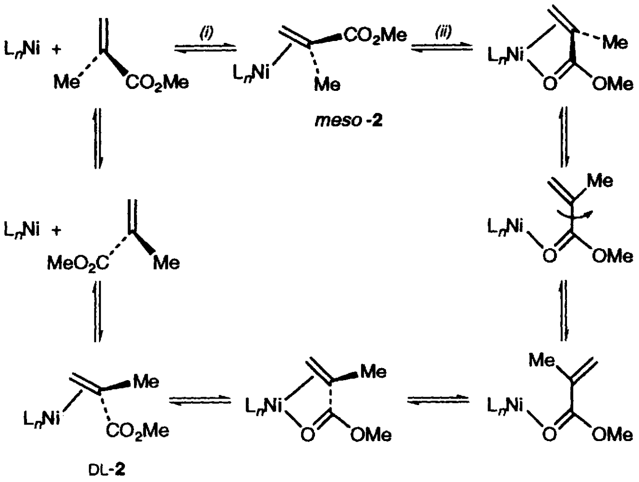
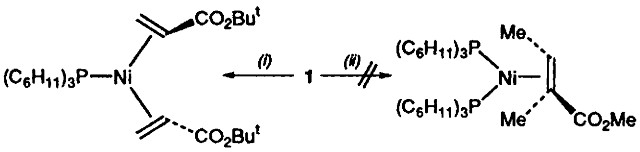


Fig. 2 Molecular structure of [Ni{η^2-CH$_2$=C(Me)CO$_2$Me}$_2$-{P(C$_6$H$_{11}$)$_3$}] **2**



Scheme 2 Possible mechanisms for the interconversion of the *meso* and DL diastereomers of **2** [L$_n$ = {CH$_2$=C(Me)CO$_2$Me}{P(C$_6$H$_{11}$)$_3$}]



4 **5**

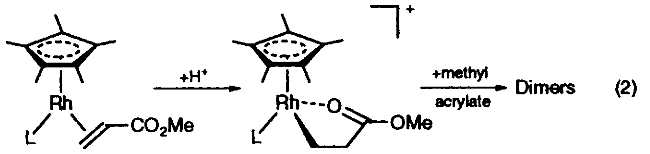
Scheme 3 Reactivity of **1** towards various alkenes. (*i*) Excess of *tert*-butyl acrylate, toluene, room temperature; (*ii*) no reaction with excess of methyl 2-methylbut-2-enoate [conditions as in (*i*)]

sised independently in procedures analogous to those used for the preparation of **1** and **2** (Scheme 1). At present, we have been unable to isolate **3** in a pure state (varying amounts of **4** are present), but the NMR spectra allow unambiguous assignment. In contrast, **1** is inert to substitution by the trisubstituted alkene methyl 2-methylbut-2-enoate. Thus the Ni$\{P(C_6H_{11})_3\}_2$ fragment bonds most strongly to the smallest alkenes, and weakly to more bulky alkenes in the following order: methyl 2-methylbut-2-enoate < methyl methacrylate < *tert*-butyl acrylate.

This is as expected on the basis of steric demand. Reaction of $[Ni(\eta^4-C_8H_{12})_2]$ with methyl methacrylate in the presence of tricyclohexylphosphine and *tert*-butyl acrylate (in 1:1:1:1 mole ratio) yielded no complexes containing co-ordinated methyl methacrylate ligands.

While **4**, like **2**, is also formed as a mixture of diastereoisomers, the DL complex is by far the major component, with the DL:*meso* ratio being 14.56:1 at room temperature (this corresponds to a ratio of 94:6). Presumably, the steric demands of the CO_2Bu^t substituents are such that the DL complex is much more stable. This is in contrast to **2**, where the *meso* diasteroisomer is the major component. Here, the geminally disubstituted methyl methacrylate ligands are not as significantly different in terms of their steric requirements, and therefore both the DL and *meso* compounds are present in significant quantities.

The 'tail-to-tail' dimerisation of methyl acrylate is catalysed by $Rh(\eta^5-C_5Me_5)$ compounds. Brookhart *et al.*[20,21] have demonstrated that the η^2-CC co-ordination of methyl acrylate precedes the coupling reaction, equation (2).



(2)

Related iridium and ruthenium O,C-chelate compounds have been recently prepared.[22] Stoichiometric and catalytic methyl acrylate dimerisation, using $[Pd(acac)_2]$–HBF_4 and $[Pd(NCMe)_4][BF_4]_2$–$LiBF_4$ mixtures respectively, has been demonstrated.[23,24] The mechanism of these reactions is rather less clear. Nevertheless, the identification of methyl methacrylate complexes of nickel as described in this paper is consistent with the proposal that the co-ordination of the carbon–carbon double bond to a late transition-metal initiates the dimerisation or polymerisation process. Further work is continuing in this area.

Conclusion

The synthesis, structure and reactivity of nickel(0) complexes containing acrylate ligands is described. The complexes adopt trigonal-planar geometries in the solid state, with the acrylate ligands η^2-CC bound. Co-ordination of two prochiral, geminally disubstituted methyl methacrylate ligands to nickel, as in **2**, results in the formation of a diastereomeric mixture with the *meso* compound the major component. Spin-saturation transfer studies indicate that the diastereomers interconvert rapidly through an intermolecular mechanism which is postulated to occur *via* an O-bound intermediate.

Experimental

All manipulations of air- and moisture-sensitive materials were carried out using standard vacuum and Schlenk techniques or in a dry-box under an atmosphere of nitrogen. All solvents were dried and purified by refluxing over a suitable drying agent, followed by distillation under a nitrogen atmosphere. Toluene was dried over molten sodium, light petroleum (b.p. 40–60 °C) and diethyl ether over sodium–potassium alloy ($NaK_{2.2}$) and tetrahydrofuran over molten potassium. The complex $[Ni(\eta^4-C_8H_{12})_2]$ was prepared using literature methods.[25] Tricyclohexylphosphine (Strem Chemicals) was used as received.

Nuclear magnetic resonance spectra were recorded using Bruker AS-250 and WH-400 spectrometers. Spectra were referenced using the resonances of residual protons in the deuteriated solvents. The variable-temperature unit was calibrated from a second thermocouple inserted in a dummy sample. Temperatures were accurate to ± 2 K. Infrared spectra were recorded using a Perkin-Elmer 1720X FTIR spectrometer. Microanalyses were obtained using a Leeman Labs CE440 analyser.

Preparations.—$[Ni\{\eta^2-CH_2{=}C(Me)CO_2Me\}\{P(C_6H_{11})_3\}_2]$ **1**. A suspension of $[Ni(\eta^4-C_8H_{12})_2]$ (0.20 g, 0.73 mmol) in diethyl ether (25 cm^3) was cooled to 0 °C. Tricyclohexylphosphine (0.41 g, 1.46 mmol) in ether (25 cm^3) was added and the mixture stirred for 15 min. An excess of methyl methacrylate (*ca.* 1.5 cm^3) was added to produce a clear orange solution. After stirring for 12 h, the solvent was removed *in vacuo*. The orange residue was extracted with toluene (30 cm^3), the solution filtered and concentrated (15 cm^3). An equal volume of light petroleum was added and the solution cooled to −30 °C to give *ca.* 0.4 g (75%) of yellow crystals of **1** [m.p. 162 °C (decomp.)].

$[Ni\{\eta^2-CH_2{=}C(Me)CO_2Me\}_2\{P(C_6H_{11})_3\}]$ **2**. To a mixture of $[Ni(\eta^4-C_8H_{12})_2]$ (0.25 g, 0.91 mmol) and $P(C_6H_{11})_3$ (0.25 g, 0.91 mmol) in diethyl ether at 0 °C was added a large excess of methyl methacrylate (*ca.* 2.5 cm^3). Work-up as above yielded *ca.* 0.3 g (60%) of large yellow crystals of **2** [m.p. 132 °C (decomp.)].

$[Ni(\eta^2-CH_2{=}CHCO_2Bu^t)_2\{P(C_6H_{11})_3\}]$ **4**. To a mixture of $[Ni(\eta^4-C_8H_{12})_2]$ (0.20 g, 0.73 mmol) and $P(C_6H_{11})_3$ (0.20 g, 0.73 mmol) in diethyl ether at 0 °C was added a large excess of *tert*-butyl acrylate (*ca.* 2.5 cm^3). Work-up as above yielded *ca.* 0.4 g (70%) of large yellow crystals of **4** [m.p. 136 °C (decomp.)].

Reaction of $[Ni(\eta^4-C_8H_{12})_2]$ *with* $CH_2{=}CHCO_2Bu^t$ *and* $P(C_6H_{11})_3$. The complex $[Ni(\eta^4-C_8H_{12})_2]$ (0.30 g, 1.07 mmol) was suspended in diethyl ether at 0 °C and $P(C_6H_{11})_3$ (0.31 g, 1.11 mmol) added. After stirring for 30 min *tert*-butyl acrylate (0.19 cm^3, 1.07 mmol) was added. Work-up as above yielded a mixture containing largely **4**, but significant quantities of $[Ni(CH_2{=}CHCO_2Bu^t)\{P(C_6H_{11})_3\}_2]$ **3**. Spectroscopic data for **3**. NMR (C_6D_6): ^1H, δ 3.16 (1 H, m, CH), 2.56 (1 H, m, CH_2), 2.1–1.0 (C_6H_{11}) and 1.62 (9 H, s, Bu^t); ^{13}C, δ 174.4 (CO_2), 76.8 (CMe_3), 44.7 (=CH), 41.6 (=CH_2) and 29.2 (Bu^t); ^{31}P, δ 38.6 [d, $J(PP')$ = 31.9] and 33.1 [d, $J(PP')$ = 31.9].

Reaction of **1** *with* $CH_2{=}CHCO_2Bu^t$. Complex **1** (25 mg, 0.03 mmol) was dissolved in deuteriobenzene and *tert*-butyl acrylate (*ca.* 0.2 cm^3) added. NMR spectra indicated that methyl methacrylate was liberated and **4** formed.

Crystal Structure Determinations.—Crystallographic data for complexes **1** and **2** are summarised in Table 7. Suitable single crystals were grown by slow cooling of toluene–light petroleum (b.p. 40–60 °C) solutions. Crystals were quickly glued to quartz fibres, coated in Nujol and cooled in the cold nitrogen gas

Table 7 Crystal data for [Ni{η^2-CH_2=C(Me)CO_2Me}$_x${P(C_6H_{11})$_3$}$_y$] (x = 1, y = 2, **1**; x = 2, y = 1, **2**)[a]

	1	**2**
(*a*) Crystal parameters		
Formula	$C_{41}H_{74}NiO_2P_2$	$C_{28}H_{49}NiO_4P$
M	719.6	539.4
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	11.667(7)	10.427(8)
b/Å	24.050(21)	12.367(12)
c/Å	14.095(7)	13.095(11)
α/°	90	113.77(9)
β/°	94.49(4)	112.23(5)
γ/°	90	90.72(7)
U/Å^3	3943	1403
Z	4	2
Crystal dimensions/mm	0.21 × 0.24 × 0.31	0.08 × 0.17 × 0.26
Colour	Yellow	Yellow
D_c/g cm^{-3}	1.212	1.277
μ(Mo-Kα)/mm^{-1}	0.61	0.78
T/K	220	200
(*b*) Data collection		
Data collected (h, k, l)	12, 25, ±15	12, ±14, ±15
Reflections collected	5456	5275
Independent reflections	5170	4977
Independent observed reflections [$F_o \geqslant 4\sigma(F_o)$]	2270	3087
Variation in standards	<0.01	<0.01
(*c*) Refinement		
R^b	0.086	0.062
$wR2^c$	0.216	0.158
Δ/σ_{max}	0.004	0.001
ρ/e Å^{-3}	0.48	0.42
$N_o/N_v{}^d$	12.4	15.4
S	0.995	0.958
Weighting scheme, $w^{-1\,e}$	$\sigma^2(F_o^2) + 0.068P^2 + 0.77P$	$\sigma^2(F_o^2) + 0.070P^2 + 0.88P$

[a] Data collected on a Siemens R3m diffractometer; graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å); $2\theta_{max}$ = 45° (**1**) or 50° (**2**); three standards every 197 reflections. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were inserted at calculated positions and fixed, with isotropic thermal parameters, U = 0.08 Å^3. [b] $R = \Sigma|F_o - F_c|/\Sigma F_o$ [for $F_o \geqslant 4\sigma(F_o)$]. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ for all data. [d] N_o = Number of observations, N_v = number of variables. [e] $P = [\max(F_o^2, 0) + 2F_c^2]/3$, where $\max(F_o^2, 0)$ indicates that the larger of F_o^2 or 0 is taken.

stream of the diffractometer. Encasing the crystal in frozen oil prevented aerial oxidation for the duration of the data collection.

Structures were solved by direct methods using SHELXTL PLUS software on a DEC Microvax-II computer. Refinements (on F^2) were carried out with SHELXL 93[26] software in an Elonex 486DX computer, minimising on the weighted R factor $wR2$. Final non-H atomic coordinates are given in Tables 2 and 5, with selected bond lengths and angles in Tables 3 and 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank ICI plc for a studentship (to A. P. J.) in support of this work, and Dr. D. Irvine (ICI plc) for useful discussions. We also thank Dr. J. J. Hastings and Dr. O. W. Howarth for help with the NMR spectroscopy.

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Received 24*th February* 1995; *Paper* 5/01129I