Design, Syntheses and Application of New Phosphine and Dithiophosphinate Complexes of Nickel: Catalyst Precursors for the Oligomerization of Ethylene

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Several new nickel(II) and nickel(0) complexes have been prepared which are active and selective for the oligomerization of ethylene to higher α-olefins. Nickel(II) complexes of the type $NiCl(PR_3)S_2PR'_2$ (R = Ph, Bu; R′ = Me, Ph) contain one bound halide ion, a monodentate phosphine, and a bidentate chelating dithiophosphinate ligand. The single-crystal X-ray structure of $NiCl(PPh_3)S_2PMe_2$ is reported. Crystal data: triclinic, space group $P\bar{1}$ (No. 2), $a = 10.288$ (2) Å, $b = 13.205$ (3) Å, $c = 16.157$ (2) Å, $\alpha = 82.63(1)°$, $\beta = 88.29(1)°$, $\gamma = 78.87(2)°$, $Z = 4$. Final R and R_w values were 0.042 and 0.048, respectively. There are two independent molecules A and B in the unit cell. In each case the molecular structure is based on a distorted square planar Ni(II) center subtended with a slightly asymmetrically bound chelated dithiophosphinate ligand with a relatively tight binding angle (S−Ni−S 87.4°). Molecule A is slightly more distorted from the square planar geometry (in that the P(V) of the dithiophosphinate chelate deviates more significantly from the coordination plane) than B. The bond distances (Ni−S (av) (trans to Cl) 2.205(2) Å, Ni−S (av) (trans to the phosphine ligand) 2.254(5) Å, Ni−Cl (av) 2.179(5) Å and Ni−P (ave) 2.021(3) Å) do not differ significantly in the two molecules. Also prepared were the nickel(0) complexes $Ni(Ph_2P−N=C(H)Ph)_4$ and $Ni(Ph_2PCH_2P(Ph_2)NC_6F_4CN)_2$. Each of the complexes is more active for the oligomerization of ethylene than are comparable conventional complexes of nickel with typical phosphine ligands. Batch reactions of the nickel complexes in combination with a 150 times molar excess of $Et_nAlCl_{3−n}$ in toluene oligomerized ethylene at temperatures below 25 °C under 0.1−2.8 MPa of ethylene and a lesser amount of inert gas. The catalyst mixtures have high activity (for example, a rate of 7.64×10^5 mol of C_2(mol of cat)$^{−1}$ h$^{−1}$ was observed for $Ni(Ph(H)NCPPh_2)_4$ with excess diethylaluminum chloride cocatalyst) and high selectivity to α-olefins, in particular 1-butene. The selectivity to 1-butene increases with increasing olefin pressure.

Introduction

Linear α-olefins, derived from basic olefins such as ethylene and propylene, are extremely useful chemicals with a large range of commercial applications, e.g., biodegradable detergents, lubricants, plasticizers, and as formulation comonomers in a wide variety of polyolefins. Their selective preparation by catalytic oligomerization of ethylene has been of significant interest to both academic and industrial chemists for many years.

The catalytic oligomerization of ethylene to yield higher α-olefins has most commonly employed complexes of titanium, nickel, and, to a lesser extent, zirconium. Much of the activity and selectivity of these complexes has been effected by the application of suitably designed ligands or ligand combinations, and by optimization of catalyst/cocatalyst (typically $Et_nAlCl_{3−n}$ or methylaluminoxane) ratios. An excellent review covering literature to 1989 summarizes the background literature concerning the development and reaction mechanisms of these catalysts.[1] Although it had appeared that a "state of the art" had been reached with nickel catalyst systems such as those used in the Shell Higher Olefins Process (SHOP),[2,3] recent interest involving subtle ligand modifications and new ligand

design shows that advancements in activity and selectivity are still attainable.[4,5] Recent development of catalysts with activities which are at least 2 orders of magnitude higher than existing commercial (e.g. SHOP) catalysts, Figure 1, have been reported.[2−7] However, in many cases these more active catalyst systems also effect isomerization of the products to the thermodynamically favored, but undesirable, internal olefins.[4] In contrast, some of the new complexes herein reported are both highly active and highly selective catalysts for the formation of 1-butene and higher α-olefins.

Many homogeneous oligomerization processes employ toluene or alkane solvents, in part because of the excellent solubility of ethylene in these solvents. However, this also requires that the catalyst precursor be soluble in this medium. To provide appropriate solubility and activity, we have constructed two types of catalyst precursors using a selection of our previously reported phosphorus−nitrogen ligands[8,9] that contain a range

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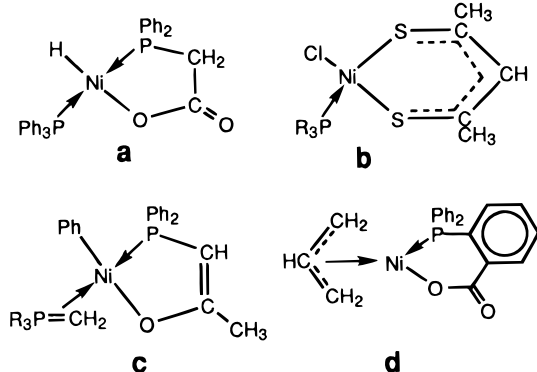
Figure 1. Some examples of effective nickel homologation catalysts. The cocatalyst is typically AlClEt$_2$ (DEAC). Compound **a** is a typical SHOP catalyst prepared from nickel(0) precursors and Ph$_2$PCH$_2$CO$_2$H or P-ylides [e.g., Ph$_3$P=CH−C(O)Ph]. See also refs 1, 5, and 7.

of aryl and alkyl organic substituents on the backbone. We have also explored the applications of nickel dithiophosphinates[10,11] and dithiophosphinates in combination with other ligands as potential catalyst precursors.
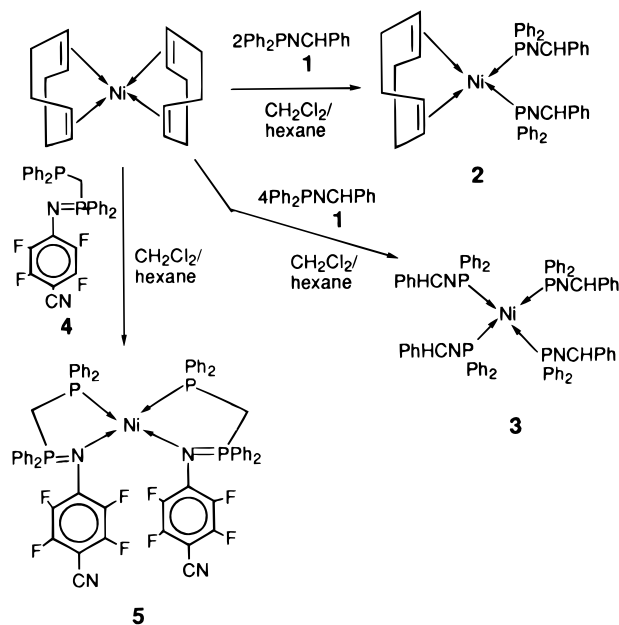
Results

(1) Preparation and Structures of Active Complexes. Nickel(0) catalyst precursors such as Ni(PPh$_3$)$_4$ are well-known and can be readily prepared from starting materials such as Ni(cod)$_2$.[12-14] Similarly, treatment of Ni(cod)$_2$ with the phosphinimine ligand Ph$_2$P−N=C(H)Ph, **1**,[9] in 2 and 4 M ratio combinations respectively yielded complexes **2** and **3** as air- and moisture-sensitive dark brown solids (Scheme 1).
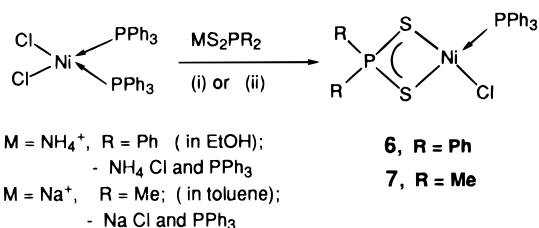
Treatment of Ni(cod)$_2$ with 2 equiv of the phosphoranimine phosphine ligand **4**[8] gave the new nickel complex **5**. In a direct comparison, complexes **2** and **3** exhibited good hydrocarbon solubility whereas complex **5** would only dissolve in warm methylene chloride and was insoluble in toluene. The poor solubility in organic solvents of metal complexes of tetrafluorocyanobenzene-substituted ligands has been noted previously.[15,16] The ^{31}P NMR spectra of complexes **2** and **3** were unremarkable, being singlets at 74.0 and 73.2 ppm, respectively. Both the solid state and solution IR spectra of **2** and **3** also show only one absorption for the C=N stretch, at 1622 and 1601 cm^{-1}, respectively, further confirming the chemical and geometrical similarities of these nickel/phosphine complexes.

The second class of complex targeted was the series of square planar nickel(II) complexes with a variety of phosphine and dithiophosphinate[10] ligands. Few complexes of this type have been reported (most examples are homoleptic),[10,11] although some structurally related analogues are known.[17,18] The synthetic path to such complexes is straightforward. Treatment of

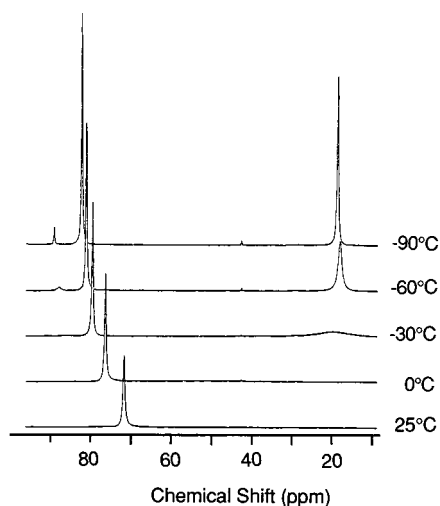(8) Katti, K. V.; Cavell, R. G. *Organometallics* **1989**, *8*, 2147−2153.
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Scheme 1

Scheme 2

NiCl$_2$(PPh$_3$)$_2$ with the dithiophosphinate salts NH$_4$S$_2$PPh$_2$ and NaS$_2$PMe$_2$ (Scheme 2) yielded the purple microcrystalline complexes **6** and **7** by elimination of NH$_4$Cl or NaCl, respectively, and PPh$_3$. Free triphenylphosphine was clearly identified (by ^{31}P{^{1}H} NMR at δ −5.8 ppm) in the reaction filtrates after removal of the product. Complexes **6** and **7** each exhibit excellent hydrocarbon solubility and are structurally similar to the less readily prepared NiCl(PR$_3$)(sacsac) complexes which are known to be highly active oligomerization catalysts.[4]
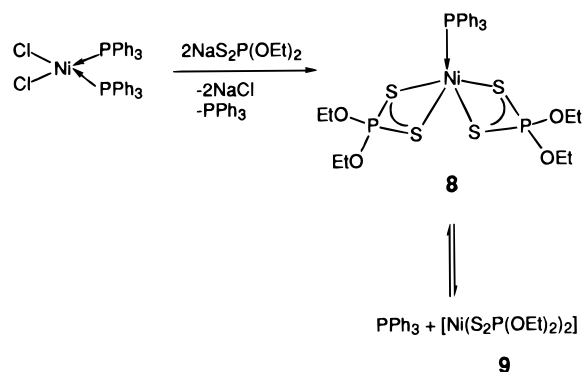
The ^{31}P{^{1}H} NMR spectra of **6** and **7** are of considerable interest. At room temperature the only resonance observed for either complex is that of the dithiophosphinate moiety at approximately δ 75−80 ppm (assigned by comparison to the ^{31}P NMR spectra of corresponding homoleptic Ni(S$_2$PR$_2$)$_2$ complexes; e.g. the ^{31}P chemical shift of an authentic[11] sample of Ni((EtO)$_2$)PS$_2$)$_2$ is +82.5 ppm). No $^3J_{PP}$ coupling was observed. The signal for the triphenylphosphine component is not visible at ordinary temperatures; however, cooling the CD$_2$-Cl$_2$ solution to −90 °C shows, as illustrated in Figure 2, the bound triphenylphosphine component. Once again, there is no conclusive evidence of $^3J_{PP}$ coupling, but both resonances are broadened. Below −90 °C the complex precipitates from solution (CD$_2$Cl$_2$ mp −97 °C). We suggest that the loss of the triphenylphosphine signal at ordinary temperatures in **6** and **7** is most likely attributable to exchange phenomenona, in particular the facile dissociation and recombination of the phosphine ligands and the participation of chelate ⇌ monomer rearrangement of the dithiophosphinate ligands. Although we cannot exclude absolutely the participation of a square planar (diamagnetic) ⇌ tetrahedral (paramagnetic) equilibrium, the fact that no EPR signal was observed for solutions of these

Figure 2. Temperature dependent $^{31}P\{^1H\}$ NMR spectra of the nickel dithiophosphinate/phosphine complex **7** in CD_2Cl_2.

Scheme 3

complexes at room temperatures where the probability of a paramagnetic species is greatest and also the fact that both the ^1H and ^{31}P NMR signals due to the dithiophosphinate moiety are not significantly broadened nor are they shifted from values typical of bound dithiophosphinates in diamagnetic square planar Ni(II) complexes suggest that the exchange process is not of this type. The possibility of the general lability of these complexes leading to active, coordinatively unsaturated complexes under catalytic conditions although not definitely established can be postulated.

Treatment of $NiCl_2(PPh_3)_2$ with 2 equiv of the diethoxydithiophosphinate ion gives the previously reported green crystalline solid complex $Ni\{S_2P(OEt)_2\}_2PPh_3$, **8**[19] (Scheme 3). This five-coordinate complex is also easily accessible by treatment of the complex $Ni\{S_2P(OEt)_2\}_2$, **9**, with PPh_3. However, the triphenylphosphine ligand in **8** is very labile, and the isolation of the pure complex (Scheme 3) requires experimental care. The broad nature of the NMR spectra of **8** makes it difficult to characterize the complex by this method; however, X-ray diffraction analysis of crystals of the product obtained from our reactions is in agreement with previously reported crystallographic data for this complex.[19]

Treatment of $NiCl_2(PBu_3)_2$ with either ammonium diphenyldithiophosphinate or sodium dimethyldithiophosphinate in toluene gave the corresponding complexes **10** and **11** as very air-sensitive purple oils (Scheme 4).

The $^{31}P\{^1H\}$ NMR spectra of **10** (R = Ph) remained broad and unresolved at all temperatures accessible using either CD_2-
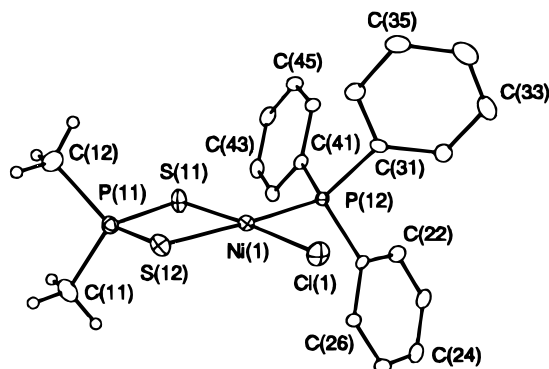
Scheme 4
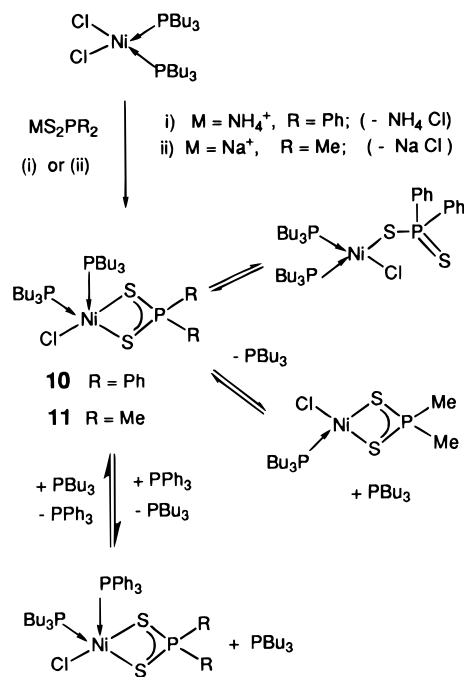
Cl_2 or toluene-d_8 as the solvent, indicating an exchange phenomenon with very low activation energy. However, the ^1H NMR spectrum was less broadened. Consequently an accurate ratio of signals for phenyl:*n*-butyl ratio could be made by integration of the ^1H NMR signals, the results of which supported the formulation of complex **10** as the bis(tri-*n*-butylphosphine)diphenyldithiophosphinate nickel chloride complex. The $^{31}P\{^1H\}$ NMR spectra of **11** exhibited two distinct and characteristic resonances in a ratio of 1:2, a sharp singlet at δ +46.8 ppm, which is indicative of a bound dithiophosphinate moiety, and a broad singlet at δ −2.0 ppm which can be attributed to two tri-*n*-butylphosphine ligands in essentially similar environments. It is suggested that the broadened nature of the NMR spectra of these complexes is due to a facile structural isomerism between square pyramidal and square planar geometries, as depicted in Scheme 4. These types of structural changes have been noted previously in nickel(II) complexes, and interchange between four-, five- and six-coordinate structures are known.[20] Further evidence of isomerism and exchange processes in these complexes was obtained by treating **11** with triphenylphosphine. At −60 °C the ^{31}P NMR spectrum of **11** showed a sharp singlet at δ +47.0 ppm (indicative of the dithiophosphinate moiety) plus several broadened signals lying between δ +5.0 and δ −15.0 ppm, suggesting an exchange process which scrambles the phosphine ligands as postulated in Scheme 4. Attempts to recover a single compound from this mixture were unsuccessful. The possibility that **10** and **11** are four-coordinate cations which exist as chloride salts has been ruled out by conductivity measurements in nitromethane solution, which showed no electrolyte character for either complex. These complexes exhibit excellent solubility in most hydrocarbon solvents, except *n*-pentane, which is attributed to the nonrigidity of the pendent hydrocarbon groups on the tris-*n*-butylphosphine ligands.

The reactions of the dithiophosphinate salts with the nickel-(II) dichloride bis(phosphine) complexes proceed smoothly and

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Figure 3. ORTEP[21] drawing for one molecule of **7** in the crystal lattice showing the atom numbering scheme. Hydrogen atoms on the phenyl rings have been omitted for clarity. Atoms are shown as 20% ellipsoids.

Table 1. Crystallographic Experimental Details for **7**

A. Crystal Data	
empirical formula	$C_{20}H_{21}ClNiP_2O_2$
fw	481.63
crystal dimensions (mm)	$0.55 \times 0.20 \times 0.08$
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters	
a (Å)	10.288 (2)
b (Å)	13.205 (3)
c (Å)	16.157 (2)
α (deg)	82.63 (1)
β (deg)	88.29 (1)
γ (deg)	78.87 (2)
V (Å³)	2135.9 (9)
Z	4
ρ_{calcd} (g cm⁻³)	1.498
μ (cm⁻¹)	13.77
B. Data Collection and Refinement Conditions	
diffractometer	Enraf-Nonius CAD4
radiation (λ [Å])	Mo Kα (0.710 73)
monochromator	incident-beam, graphite crystal
temperature (°C)	−50
takeoff angle (deg)	3.0
detector aperture (mm)	$(3.00 + \tan \theta)_{horiz} \times 4.00_{vert}$
crystal-to-detector distance (mm)	173
scan type	$\theta - 2\theta$
scan rate (deg min⁻¹)	6.7−1.4
scan width (deg)	$0.60 + 0.344 \tan \theta$
data collection 2θ limit (deg)	50.0
total data collected	7756 ($\pm h, \pm k, +l$)
range of absorption correction factors	0.8281−1.1395
total no. of unique data	7408
no. of observations (*NO*)	3994 ($I > 3\sigma(I)$)
final no. of parameters varied (*NV*)	469
R[a]	0.042
R_w[b]	0.048
GOF[c]	1.209

[a] $R = \sum ||F_o| - |F_c||/\sum |F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [c] GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

efficiently in most solvents tested, even though both reactants are in apparent suspension. We have found that certain solvent combinations give good yields of the complexes, as noted in the Experimental Section.

X-ray structure quality single crystals of the complex **7** were obtained by slow diffusion of hexane into a saturated dichloromethane solution of the complex. An ORTEP[21] view of the molecule with atom labeling is shown in Figure 3. Experimental crystal analysis parameters and selected metrical results are given in Tables 1 and 2. Although there are two independent

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Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **7**

molecule A		molecule B	
Ni(1)−Cl(1)	2.175(2)	Ni(2)−Cl(2)	2.183(2)
Ni(1)−S(11)	2.205(2)	Ni(2)−S(21)	2.206(2)
Ni(1)−S(12)	2.259(2)	Ni(2)−S(22)	2.249(2)
Ni(1)−P(12)	2.187(2)	Ni(2)−P(22)	2.183(2)
S(11)−P(11)	2.022(2)	S(21)−P(21)	2.019(2)
S(12)−P(11)	1.991(2)	S(22)−P(21)	2.002(2)
P(11)−C(11)	1.800(7)	P(21)−C(51)	1.787(6)
P(11)−C(12)	1.781(7)	P(21)−C(52)	1.784(7)
P(12)−C(21)	1.832(5)	P(22)−C(61)	1.809(5)
P(12)−C(31)	1.809(6)	P(22)−C(71)	1.817(6)
P(12)−C(41)	1.830(5)	P(22)−C(81)	1.821(5)
Cl(1)−Ni(1)−S(11)	177.53(9)	Cl(2)−Ni(2)−S(21)	176.38(8)
Cl(1)−Ni(1)−S(12)	90.44(7)	Cl(2)−Ni(2)−S(22)	89.71(7)
Cl(1)−Ni(1)−P(12)	88.55(6)	Cl(2)−Ni(2)−P(22)	89.43(7)
S(11)−Ni(1)−S(12)	87.44(6)	S(21)−Ni(2)−S(22)	87.98(7)
S(11)−Ni(1)−P(12)	93.71(6)	S(21)−Ni(2)−P(22)	93.03(7)
S(12)−Ni(1)−P(12)	172.64(7)	S(22)−Ni(2)−P(22)	176.66(7)
Ni(1)−S(11)−P(11)	86.04(8)	Ni(2)−S(21)−P(21)	86.00(8)
Ni(1)−S(12)−P(11)	85.32(8)	Ni(2)−S(22)−P(21)	85.26(8)
S(11)−P(11)−S(12)	100.53(9)	S(21)−P(21)−S(22)	100.6(1)
S(11)−P(11)−C(11)	113.2(3)	S(21)−P(21)−C(51)	112.5(2)
S(11)−P(11)−C(12)	110.9(3)	S(21)−P(21)−C(52)	111.1(2)
S(12)−P(11)−C(11)	111.6(3)	S(22)−P(21)−C(51)	112.2(3)
S(12)−P(11)−C(12)	114.2(3)	S(22)−P(21)−C(52)	114.7(3)
C(11)−P(11)−C(12)	106.5(4)	C(51)−P(21)−C(52)	106.0(3)
Ni(1)−P(12)−C(21)	119.0(2)	Ni(2)−P(22)−C(61)	114.2(2)
Ni(1)−P(12)−C(31)	106.3(2)	Ni(2)−P(22)−C(71)	109.8(2)
Ni(1)−P(12)−C(41)	109.1(2)	C(61)−P(22)−C(71)	108.3(3)
C(21)−P(12)−C(41)	100.8(2)	C(61)−P(22)−C(81)	101.8(3)
C(31)−P(12)−C(41)	104.2(2)	C(71)−P(22)−C(81)	105.1(3)
P(12)−C(21)−C(22)	119.8(4)	P(22)−C(61)−C(62)	120.6(4)
P(12)−C(21)−C(26)	120.9(4)	P(22)−C(61)−C(66)	120.7(4)
P(12)−C(31)−C(32)	125.1(4)	P(22)−C(71)−C(72)	124.4(5)
P(12)−C(31)−C(36)	116.6(4)	P(22)−C(71)−C(76)	116.8(5)
P(12)−C(41)−C(42)	118.2(4)	P(22)−C(81)−C(82)	118.4(4)
P(12)−C(41)−C(46)	122.7(4)	P(22)−C(81)−C(86)	123.0(4)

molecules in the unit cell, the molecular structures are similar, being derivatives of the typical Ni(II) square planar structure. In molecule A, the P(V) of the dithiophosphinate chelate deviates more significantly from the coordination plane and thus is slightly more distorted from the square planar geometry than is the case for B, but otherwise the structures are very similar and the bond distances comparable. In both cases the nickel center displays a slightly distorted square planar coordination because of the tight bite angle of the chelated dithiophosphinate ligand (S−Ni−S 87.4°) and the action of the bulky triphenylphosphine ligand (S−Ni−P 93.7°). However, smaller dithiophosphinate chelate bite angles of 82.06(6)° have been observed in other nickel(II) bis(dithiophosphinato) complexes[22−24] and angles as tight as 75.2(1)° have been reported for other metals,[25] so the deviations are not unusual. The Ni−S bond lengths, which are in the range 2.21−2.26 Å, are comparable with those found for other square planar four-coordinate Ni(II) dithiophosphinate complexes such as Ni[S₂P(OCy)₂]₂ (2.22 Å).[22−24]

(2) Catalytic Activity. Preliminary Screening. The reported complexes were first tested for oligomerization activity in the presence of ethylene at 1 atm, with diethylaluminum chloride (DEAC) as cocatalyst. These screening tests were

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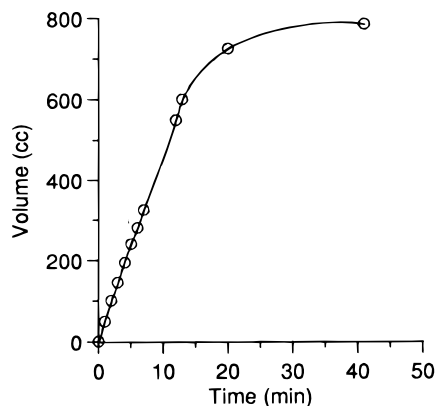
Figure 4. Low-pressure (1 atm) uptake of ethylene at 23 °C by a catalyst system formed from complex **11** and DEAC in toluene (initial rate: 1090 mol of C_2H_4 per mol of Ni per h).

designed to provide an indication of the most reactive systems, and, although oligomerization catalysts are generally used under pressures in excess of 3 MPa, it was considered that any catalyst of potential value in industrial applications would show some activity at low pressure, thus by this approach relatively less active complexes could be rejected. Although this process improves the efficiency of catalyst testing, there always remains the possibility that a system that is seemingly uninteresting at low pressures will become highly catalytically active at the very much higher pressures typical of operational use. The fluoro-aromatic substituted complex **5** had such poor solubility in toluene that it was not considered as a viable catalyst candidate. The PNC complexes **2** and **3** showed excellent solubility but low activity under 1 atm of ethylene. In contrast, the dithio-phosphinate-substituted complexes **6**−**11** each exhibited moderate to high activity under 1 atm pressure of ethylene at 23 °C, with the methyl-substituted dithiophosphinate complex **11** giving an initial turnover rate of 1090 mol of ethylene per mole of complex per hour, Figure 4. Complexes giving encouraging results were selected for more detailed screening, including product analysis.

High-Pressure Tests. Comparative tests for activity and selectivity were performed for those materials passing the initial screening. These comparative tests were performed at an ethylene partial pressure of 1.6 MPa, an initial temperature of 15 °C, and a DEAC to nickel ratio of 150:1. The ethylene uptake rate is considered to be the overall rate of reaction. A plot of the ethylene flow rate against time was fitted to an exponential curve and extrapolated to zero time in order to establish the initial rate of reaction (Figure 5). Due to a rapid and often large initial exotherm, isothermal data for the early portion of the experiment were not available. The ethylene flow rates for complexes **6** and **7** exceeded the flowmeter maximum (i.e. 20 dm^3/min). The process is very exothermic, and the temperature rises rapidly to a value 30−55 °C above the initial setpoint. In earlier tests, we had observed a deterioration of catalyst lifetime at elevated temperatures and surmised that the catalyst was heat-sensitive. Consequently, only rough estimates could be made for the initial rates [(2−8) × 10^6 mol/mol h] for these two catalyst systems. It is interesting to note that the immediate coordination environment about Ni in complexes **6** and **7** is very similar to those reported by Masters et al.[26] for systems which provided catalyst activities in excess of 3.0 × 10^6 mol/mol h. Furthermore, varying the phosphine substituents

(26) Brown, S. J.; Masters, A. F. *J. Organomet. Chem.* **1989,***367*, 371−374.
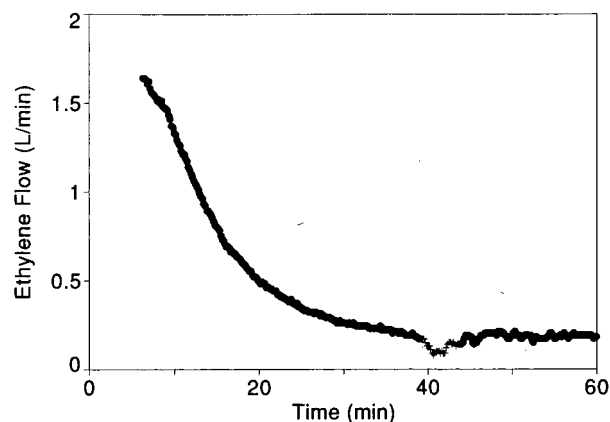
Figure 5. Uptake of ethylene by a catalyst solution formed by complex **11** and DEAC.

Table 3. Product Distributions for Selected Catalyst Precursor Complexes

compd no.	C_4	C_6	C_8	$1\text{-}C_4$	*cis*- $2\text{-}C_4$	*trans*-$2\text{-}C_4$
3	95.26	3.69	0.44	83.16	5.41	6.69
6	93.14	6.02	0.41	52.19	17.39	23.55
7	83.81	4.87	2.53	21.85	29.04	32.92
8	94.41	4.33	0.41	57.21	17.00	20.20
9	76.31	12.11	10.19	69.11	2.45	4.75
10	87.33	4.90	7.09	22.59	28.57	36.17
11	96.21	2.08	0.24	41.26	25.72	29.23

Table 4. Comparative Studies on Selected Nickel Catalyst Precursors

compd no.	rate × 10^5, mol/mol h	$1\text{-}C_4/\Sigma C_4$, wt %	$C_4/\Sigma C$,[b] wt %
3	7.64[a]	87.30	95.26
6	26[c]	56.03	93.14
7	89[c]	26.07	83.81
8	6.45	60.60	94.41
9	2.82	90.56	76.31
10	13.2	25.87	87.33
11	12.8	42.88	96.21

[a] At 2.8 MPa. [b] ΣC = total product. [c] Estimate.

affects only the catalyst activity whereas varying the substituents on the chelate affected both the activity and the selectivity.[26] Keim[3] has suggested that catalytic activity in this system requires that the nickel be in the +1 oxidation state, in a square planar environment, and that the complex must contain a chelating ligand. Preferably, one of the remaining ligands is labile, to facilitate the formation of a vacant coordination site. Under these circumstances, the chelate controls both catalyst activity and selectivity while the relatively nonlabile ligand affects only the overall activity of the catalyst.

The initial rates and selectivities for the catalyst systems described herein, determined both as the weight fraction of 1-butene in the C_4 stream and as the weight fraction of the C_4 stream in the total product slate, are given in Tables 3 and 4. These results are consistent with those reported by Keim et al.[7] and Brown and Masters[26] for related systems similar in some respects to **6** and **7**. It appears that in these four coordinate complexes the aliphatic dithiophosphinates provide a more active but less selective catalyst while in five-coordinate complexes (cf. **10** and **11**) the reverse applies. It is therefore surprising that **9** shows such high activity and selectivity in apparent contravention of Keim's postulates.[7] Even more surprising is that the coordination of triphenylphosphine to **8** would yield a more active catalyst. Consistent with the findings of Keim,[7]
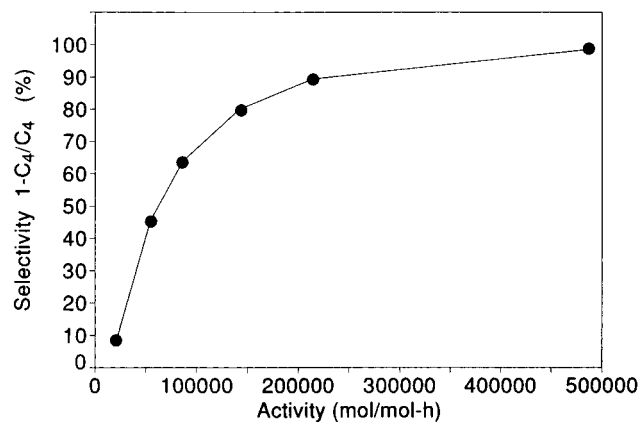
Figure 6. Correlation of selectivity and reactivity with ethylene pressure for the catalytic system formed from **3** and DEAC. The activity−pressure relationship is given in Table 5.

Table 5. Dependence of Activity on C_2H_4 Pressure[a]

C_2H_4 press, psig	activity, mol/mol h	$1-C_4/\Sigma C_4$
30	18 155	9.4
60	62 586	46.1
110	87 983	67.0
215	114 948	82.9
400	214 517	87.3
2000	540 389	98.2

[a] For the catalytic system formed from **3** and DEAC.

however, the addition (i.e. coordination) of triphenylphosphine shifts the product distribution to the shorter carbon oligomers.

In contrast to the behavior of the related system,[26] we do not find isomerization of the 1-butene products to be faster than ethylene oligomerization. In all cases, the present system provides an amount of 1-butene in the C_4 fraction which is greater than expected from thermodynamics. Moreover, there is a relationship between this selectivity and activity (Figure 6) which is not intuitively obvious. We have observed that both the overall reaction rate and the selectivity to 1-butene increase with the ethylene partial pressure (Table 5). Thus it may be postulated that isomerization is not intimately associated with the oligomerization reaction and that the rate of product isomerization is considerably less than that of the ethylene oligomerization process. However, 1-butene, the primary product of oligomerization, undergoes slow isomerization to *cis*- and *trans*-2-butene when in contact with the catalyst. Support for the above postulate was obtained by contacting 1-butene with complex **6** at 15 °C. Of the total product obtained, 83.6 wt % was the collection of butene isomers and the remainder was octenes. The butene distribution was 2.2% 1-butene, 72.1% *cis*-2-butene, and 25.7% *trans*-2-butene.

Conclusions

Several new nickel complexes in conjunction with common cocatalysts such as DEAC provide active and selective catalysts for the oligomerization of ethylene to 1-butene. Either Ni(II) or Ni(0) complexes may be used, the former being more active but the latter being more selective. It is notable that the complex Ni(Ph₂PNC(H)Ph)₄ shows unusually high selectivity for oligomerization to α-olefins in contrast to previously evaluated complexes based on standard phosphines, indicating the enhancements in activity which can accrue from the modification of the ligands alone. Unlike other comparable highly active oligomerization systems, isomerization does not play an influential role in the catalytic cycles of the present systems.

Experimental Section

Solvents were dried and distilled prior to use, and manipulations were carried out using standard Schlenk techniques under an argon atmosphere. NMR spectra were taken on a Bruker 200 MHz instrument operating at 81.015 MHz for ³¹P referenced to H_3PO_4 and at 200.133 MHz for ¹H referenced to $SiMe_4$. Spectra were measured relative to the ²H lock of the internal deuterated solvent. Positive shifts lie downfield in all cases. Infrared spectra were taken on a Fourier transform instrument using both microscope and dichloromethane cast techniques. Mass spectra were taken using fast atom bombardment, and the resultant ions were detected with a positive ion detector. Microanalyses were carried out in the Department of Chemistry Microanalytical Laboratory of the University of Alberta. The ligands $Ph_2PNCHPh$ (**1**)[9] and $Ph_2PCH_2P(Ph_2)NC_6F_4CN$ (**4**)[8] were prepared as previously described. $NaS_2PMe_2 \cdot 2H_2O^{27}$ was also prepared as previously described. The salt $NH_4S_2PPh_2$ was prepared by treating a toluene solution of Ph_2PS_2H with gaseous ammonia until precipitation of the product occurred.[27]

Initial Screening for Catalytic Activity. A solution of the appropriate complex (4×10^{-4} mol in 100 cm³ of toluene) was prepared in a 200 cm³ Schlenk flask containing a magnetic stirrer. The flask was fitted to a standard hydrogenation apparatus comprising a 500 cm³ buret and bulb filled with ${}^iPrOH$/glycerol ballast, a mercury manometer, and a vacuum/gas inlet tap. The system was then evacuated and purged three times with ethylene. The solution was then stirred vigorously until the ethylene had equilibrated with the toluene solvent. At this point, diethylaluminum chloride solution (2 cm³, 1.8 M) was introduced to the reaction vessel and the timing of the reaction started. Ethylene uptake, indicated by upward movement of the ballast solution in the buret, was measured at 1-min intervals until catalytic activity declined.

Parametric Experiments. All high-pressure ethylene oligomerization tests were performed in a 1-dm³ Parr autoclave fitted with a Magnadrive stirrer assembly. The reactor was preconditioned prior to use by injecting 2 cm³ of cocatalyst (25 wt % in toluene) into the reactor containing about 500 cm³ of toluene and stirring for at least 1 h (overnight preferred). (This procedure removes any oxygen, moisture, and any other potential reaction poisons adsorbed on the reactor walls. Variable reactivity results are often obtained if such preconditioning is not done.) After this preconditioning solution was removed from the reactor, the reactor was rinsed with fresh toluene, dried, flushed with N_2, and loaded with 200 cm³ of degassed toluene. The reactor was then brought to reaction pressure with ethylene. The appropriate amount of cocatalyst dissolved in toluene (10 cm³) was injected using an injection bomb (internal volume 30 cm³) pressurized to 5.6 MPa with purified N_2. The reactor contents were stirred for 5 min before the catalyst solution (10 cm³) was similarly injected. The reactor was operated in the semibatch mode at constant pressure with ethylene being fed on demand. The rate of ethylene consumption and the total amount of ethylene fed to the reactor were measured using a precalibrated mass flowmeter and recorded automatically, as were continuous temperature and pressure readings, by use of Labtech Notebook. The reaction was terminated by injecting 10 cm³ of water in the same manner as the catalyst and cocatalyst solutions. The volume of gaseous products leaving the reactor at the end of the run was measured using a wet test meter corrected to STP. These gases were collected and analyzed by gas chromatography (GC, HP 5890 series II, 10 ft. × ¹/₈ in. Porapak R, 80/100 mesh, 50 °C for 8 min then 10 °C/min to 250 °C) to determine the total amount of ethylene consumed. The reactor contents were drained and weighed, and an aliquot was analyzed by gas chromatography (HP 5890 series II, 50 m × 0.2 mm PONA 50 μm liquid phase, 30 °C for 8 min then 5 °C/min to 250 °C). The results of the gas and liquid analyses were combined to determine the product distribution (Table 3).

Nickel(0) Catalyst Precursors. $Ni(Ph_2P-N=C(H)Ph)_4$ (3). Bis-(1,5-cyclooctadiene)nickel (0.48 g, 1.76 mmol) and $Ph_2P-N=C(H)$-Ph (2.023 g, 6.99 mmol) were stirred as a suspension in hexane in a flask under an argon atmosphere at 0 °C. Dichloromethane was slowly added to the suspension until dissolution occurred, whereupon a brown

(27) Day, E. D. Ph.D. Thesis, University of Alberta, 1972.

precipitate immediately formed. The mixture was allowed to warm to room temperature, and the precipitate was filtered and dried under vacuum to give **1** as a product sensitive to both air and moisture. NMR: ^{31}P (81 MHz), δ 74.0 ppm (vs H_3PO_4); ^{1}H (200 MHz), δ 6.8–8.1 (m, Ph and CH) ppm. IR $\nu_{(C=N)}$: 1622 cm^{-1}. MS (FAB) (%): NiL$_4$, 1216 (0.3), NiL$_3$, 927 (6.4), NiL$_2$, 638 (18.5), NiL, 349 (12.4). Anal. Found: C, 72.6; H, 5.3; N, 4.2. Calcd for C$_{76}$H$_{64}$N$_4$NiP$_4$: C, 72.9; H, 5.4; N, 4.5.

Ni(cod)(Ph$_2$P—N=C(H)Ph)$_2$ (2). Bis(1,5-cyclooctadiene)nickel (1.377 g, 5 mmol) and Ph$_2$P—N=CHPh (2.9 g, 10 mmol) were stirred as a suspension in hexane in a flask under an argon atmosphere at 0 °C. Dichloromethane was slowly added to the suspension until solution occurred, and immediately a brown precipitate formed. The mixture was allowed to warm to room temperature, and the precipitate was filtered and dried under vacuum to give **2** as a product sensitive to both air and moisture. NMR: ^{31}P (81 MHz), δ 73.2 ppm; ^{1}H (200 MHz), δ 2.5 (m, cod), 5.5 (m, cod olefinic), 7.0–8.1 (m, Ph) ppm. IR $\nu_{(C=N)}$: 1601 cm^{-1}. MS (FAB) (%): [NiL$_2$(cod)]–Ph, 669 (18.6), Ni(cod), 166.8 (22.0) Ph$_2$PNH$_2$, 201 (51.0). Anal. Found: C, 72.6; H, 3.6; N, 5.5. Calcd for C$_{46}$H$_{44}$N$_2$NiP$_2$: C, 72.3; H, 3.6; N, 6.0.

Ni(Ph$_2$PCH$_2$P(Ph)$_2$=N—C$_6$F$_4$CN)$_2$·CH$_2$Cl$_2$ (5). Bis(1,5-cyclooctadiene)nickel (0.387 g, 1.4 mmol) and Ph$_2$PCH$_2$P(Ph)$_2$N-C$_6$F$_4$CN (1.53 g, 2.67 mmol) were stirred as a suspension in hexane (15 cm^3) in a flask under an argon atmosphere at 0 °C. Dichloromethane (5 cm^3) was slowly added to the suspension until a brown solution formed, from which a red precipitate was subsequently formed. The mixture was allowed to warm to room temperature, and the precipitate was filtered and dried under vacuum to give **5** as an analytically pure product. MS (FAB) (%): NiL, 630.6 (3.1), L, 573 (4.8). Anal. Found: C, 60.4; H, 3.6; N, 4.1. Calcd for C$_{65}$H$_{46}$N$_4$F$_8$NiP$_4$: C, 60.5; H, 3.6; N, 4.3.

Nickel(II) Dithiophosphinate Complexes. NiCl(PPh$_3$)(S$_2$PPh$_2$) (6). A mixture of NiCl$_2$(PPh$_3$)$_2$ (1.645 g, 2.5 mmol) and NH$_4$[S$_2$PPh$_2$] (0.672 g, 2.5 mmol) in ethanol (150 cm^3) was stirred under argon for 0.5 h. Diethyl ether (50 cm^3) was added to the resulting solution, and the mixture was stirred for a further 10 min, after which the solution was filtered and washed with degassed diethyl ether (3 × 20 cm^3). CH$_2$Cl$_2$ (150 cm^3) was then added to the filtrate, and the resulting mixture was further filtered to remove any inorganic salts. The product was recrystallized using a mixture of CH$_2$Cl$_2$/hexane. Yield: 1.18 g (76%). Mp 140–155 °C, decomp. NMR: ^{31}P (CD$_2$Cl$_2$) (81 MHz) (−90 °C), δ 77.8 (br, s), 19.9 (br, s) ppm; ^{1}H (200 MHz), δ 7.0–8.0 (m, Ph) ppm. MS (FAB) (%): M − Cl, 570 (26), NiS$_2$PPh$_2$, 308 (12). Anal. Found: C, 60.2; H, 4.1; Cl, 5.5; S, 10.9. Calcd for C$_{70}$H$_{25}$-ClNiP$_2$S$_2$: C, 59.5; H, 4.1; Cl, 5.9; S, 10.6.

NiCl(PPh$_3$)(S$_2$PMe$_2$) (7). A mixture of NiCl$_2$(PPh$_3$)$_2$ (10.00 g, 15 mmol) and NaS$_2$PMe$_2$·2H$_2$O (2.67 g, 15 mmol) in toluene (300 cm^3) was stirred under argon for 2.5 h. The solution was cooled to −20 °C and filtered, and then the solid residue was washed with degassed diethyl ether (3 × 20 cm^3) and dried under vacuum for 0.5 h. CH$_2$Cl$_2$ (150 cm^3) was added to the filtrate, and the resulting mixture was further filtered to remove any inorganic salts. The compound was then recrystallized using a mixture of CH$_2$Cl$_2$/hexane. Yield: 5.85 g (81%). NMR: ^{31}P (CD$_2$Cl$_2$) (81 MHz) (−90 °C), δ 82.3 (s, br), 19.8 (s, br) ppm. ^{1}H (200 MHz), δ 7.3–7.8 (m, Ph), 1.9 (d, CH$_3$, J_{PH} = 12.0 Hz) ppm. MS (FAB) (%): M − Cl, 446 (79), Ni(S$_2$PMe$_2$), 184 (97). Anal. Found: C, 50.25; H, 4.28; S, 13.37; Cl, 7.39. Calcd for [NiCl-(PPh$_3$)(S$_2$PMe$_2$)]: C, 49.9; H, 4.36; S, 13.3; Cl, 7.4.

Ni(PPh$_3$)[S$_2$P(OEt)$_2$]$_2$ (8). A mixture of NiCl$_2$(PPh$_3$)$_2$ (1.00 g, 1.5 mmol) and NH$_4$[S$_2$P(OEt)$_2$] (2.76 g, 1.5 mmol) in dichloromethane (150 cm^3) was stirred under argon for 0.5 h. The solution was filtered to remove inorganic salts. The dichloromethane was removed under vacuum, and the resulting solid was redissolved in diethyl ether (20 cm^3). Slow evaporation of the solvent to approximately 5 cm^3 at room temperature resulted in the precipitation of the desired product. The compound was recrystallized using this method to remove any excess PPh$_3$ and was identified by comparison with the literature data.[19] Yield: 0.69 g 65%. NMR: ^{31}P (CD$_2$Cl$_2$) (81 MHz), δ 40 (br) ppm; ^{1}H (200 MHz), δ 7.2–7.5 (m, Ph), 4.3 (m, CH$_2$), 1.4 (t, CH$_3$) ppm. MS (FAB) (%): M, 692 (51), Ni(PPh$_3$)$_2$, 583 (43), [Ni(S$_2$P(OEt)$_2$)$_2$], 429 (36).

NiCl(PBu$_3$)$_2$(S$_2$PPh$_2$) (10). A mixture of NiCl$_2$(PPh$_3$)$_2$ (1.657 g, 3 mmol) and NH$_4$[S$_2$PPh$_2$] (0.802 g, 3 mmol) in toluene (150 cm^3) was stirred under argon with for 0.5 h. The solution was then filtered to remove inorganic salts. The toluene was removed under reduced pressure to quantitatively yield the product as an extremely air-sensitive purple oil. NMR: ^{31}P (CD$_2$Cl$_2$) (81 MHz), very broad at all temperatures; ^{1}H (200 MHz) 6.9–8.1 (m, br, Ph), 0.7–1.8 (m, br, Bu).

NiCl(PBu$_3$)$_2$(S$_2$PMe$_2$) (11). A mixture of NiCl$_2$(PBu$_3$)$_2$ (1.657 g, 3 mmol) and NaS$_2$PMe$_2$·2H$_2$O (0.553 g, 3 mmol) in toluene (150 cm^3) was stirred under argon for 2 h. The solution was then filtered to remove inorganic salts. The toluene was removed under reduced pressure to give a high (80–90%) yield of the product as an extremely air-sensitive purple oil. NMR: ^{31}P (CD$_2$Cl$_2$) (81 MHz), δ 46.8 (s, P), −2.0 (s, br, 2P) ppm; ^{1}H (200 MHz), δ 0.7–1.9 (m, br, alkyl) ppm.

Supporting Information Available: Complete experimental details, tables of atom coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for the crystal structure of **7** (21 pages). Ordering information is given on any current masthead page.

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