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Reaction of nickel polymerization catalysts with carbon monoxide

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Abstract

The nickel compound, $Ni(Ph_2PCH{=}C(Ph)O)(PEt_3)Ph$, is a catalyst precursor for ethylene homopolymerization and the alternating copolymerization of ethylene with carbon monoxide. In the absence of ethylene, CO is a catalyst poison. In an effort to understand the mechanisms of these reactions, we have investigated the chemistry of the compounds with pure CO. The crystal structures of the catalyst precursor and the benzoyl product resulting from the insertion of CO into the Ni–Ph bond are presented. Several zero-valent complexes of Ni and an organic product based on the coupling of the chelating ligand and the benzoyl group have been isolated and characterized. A brief description of the polymerization mechanism is presented.

Introduction

The alternating copolymerization of CO [1,2] with ethylene has intrigued polymer scientists for some time. Sen has investigated the reaction employing "naked palladium" [3] catalysts and has reviewed much of the relevant literature [4]. In the course of our investigation of the copolymerization of ethylene with polar monomers using nickel catalysts derived from ylid **1** and related species, we discovered that these nickel catalysts would catalyze the rigorously alternating 1/1 ethylene/CO copolymerization under certain circumstances. The unusual feature of these copolymerizations is that the polymerization must be initiated in the absence of CO which poisons the catalyst precursor. Once the polymerization has been initiated, the CO can be admitted to the ongoing polymerization and the polymer formed from that point on is the alternating copolymer. Thus the polymer chains are

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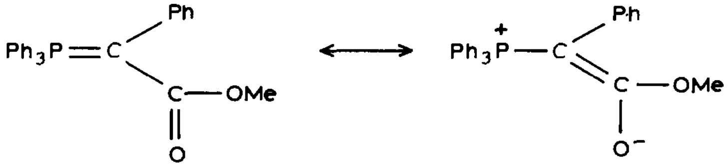
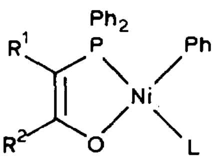
sequential blocks of polyethylene followed by ethylene/CO. These unique polymers are the subject of a separate publication in this series [5].



(1)

The catalysts, **2**–**5**, used in this study, are of the same general class as those which form the basis for the well-known SHOP process whereby Shell oligomerizes ethylene to higher olefins [6,7]. More recently [8], the catalysts have been shown to homopolymerize ethylene to high molecular weight, high density polyethylene (HDPE) when there is no phosphine ligand, L, in the fourth coordination site of these square planer species. The vacant coordination can be "lightly stabilized" with a ligand such as pyridine which is a good leaving group, or by the dimerization of two of the coordinatively unsaturated complexes through oxygen bridges.

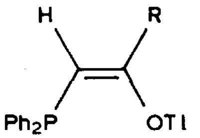


	R^1	R^2	L
2	Ph	OMe	PEt_3
3	Ph	OMe	PPh_3
4	H	Ph	PEt_3
5	H	Ph	PPh_3

We have been investigating the use of these catalysts to prepare functionalized linear low density polyethylene (FLLDPE) by the copolymerization of ethylene with functionalized polar monomers [9]. Such monomers are catalyst poisons for normal Ziegler-Natta catalysts, though the expected polymers have been prepared experimentally by deactivating the polar groups with a large excess of aluminum alkyl and carrying out the polymerization in a normal Ziegler–Natta manner. Commercial polymers of this type are prepared by very high pressure, free radical copolymerization [10] which yields functionalized low density polyethylene (FLDPE). These polymers fill an important, high-value niche in the polymer industry. Examples of commercial products are in the Vamac®, Elvax®, and Surlyn® resins which are ethylene/vinyl acetate, ethylene/acrylic, and an ionomerically crosslinked ethylene/acrylic acid, respectively. It would be of considerable interest to the industry to be able to prepare these functionalized copolymers by a low pressure route from monomers as inexpensive as CO; such a process would lead to considerable savings in the initial investment in equipment and in the operating costs of the process.

Results and discussion

The chelated nickel complexes, **2**–**5**, are readily prepared by the oxidative addition of the appropriate phosphorus(V) alkylidenephosphoranes to bis(1,5-cyclooctadiene)nickel(0) in the presence of a tertiary phosphine. This procedure, which yields the phenyl derivative of the phosphine chelate complex, has been detailed in a number of publications [6,11]. Alternatively, the phosphorus(III)



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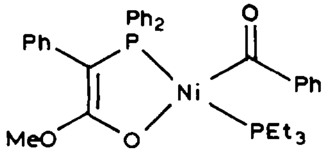


(7)

species, **6**, can be added to preformed nickel(II) species to give a variety of catalysts or catalyst precursors [12].

It was of interest to investigate further the nature of the reactions of these chelated nickel complexes with carbon monoxide. Compound **2** reacts rapidly and reversibly with carbon monoxide to give the benzoyl species, **7**. Keim [13] has reported CO insertion in a closely related complex. The observed rate of reaction is much faster than the observed rate initiation of polymerization in ethylene homopolymerization. Thus, CO insertion takes place more rapidly than ethylene insertion. The 600 MHz ^1H NMR spectrum of **7** shows diastereotopic methylene protons in the PEt_3 ligand. They appear as a pseudo-octet at 1.17 ppm and a pseudo-heptet at 1.34 ppm with a 7 Hz separation between the lines. On heating to 50 ° C, the two multiplets begin to coalesce, and this behavior is reversed if the temperature is lowered. The room temperature $[^1H]^{31}P$ NMR spectrum is an AB spin system with very second-order doublets at 19.23 and 17.65 ppm (J(PP) 198 Hz) and is invarient on heating to 80 ° C. This NMR behavior is consistent with a hindered rotation of the benzoyl group creating a top and bottom side to the complex. This solution structure was confirmed in the solid state by an X-ray crystallographic determination.

The details of the structural determination of compound **7** and also of compound **2** which was done for comparison, are tabulated in Table 1. The results for complexes **2** and **7** are tabulated in Tables 2 and 3. Perspective views of the two complexes are shown in Figures 1 and 2. Selected bond distances and angles are compiled in Table 4. Both of the complexes adopt the square planar geometry expected for nickel(II). The phosphorus ligands are *trans* to one another in both complexes. The chelate ring is planar in each of the complexes, and the delocalization of the π-system which has been noted previously [13] is once again observed. The delocalization is reflected in the ring distances and angles. Minor differences between the corresponding parameters in complexes **2** or **7**, and complex **5** [14] presumably result from the increased bulk of the triphenylphosphine ligand and the differing chelate substitution patterns. There are only minor differences between the inner coordination parameters of complexes **2** and **7**. A slight elongation of the Ni–O(1) distance upon carbonylation is accompanied by small decreases in the chelate ring distances, possibly indicating increased delocalization. Also note the lack of conjugation between the chelate ring and the attached phenyl rings in complex **7** (50 ° dihedral angle) which is in contrast to complex **2** in which these groups are nearly coplanar. In both complexes, the phenyl or benzoyl group is oriented perpendicularly to the coordination plane. Close intermolecular contacts suggest that rotation about the Ni–C bond would be unfavorable. It is this impediment to rotation of the benzoyl group in complex **7** which gives rise to the observed diastereotopism of the PEt_3 methylene resonances in the ^1H NMR

Table 1

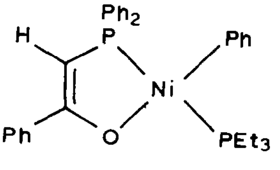
Summary of X-ray diffraction data

	2	7
Complex	Ni(Ph$_2$PC(Ph)=C(OMe)O)(PEt$_3$)(Ph)	Ni(Ph$_2$PC(Ph)=C(OMe)O)(PEt$_3$))(COPh)
Formula	$C_{33}H_{38}NiO_2 \cdot 1/2(C_7H_8)$	$C_{34}H_{38}NiO_3P_2$
f_w	587.33	615.34
space group	$P2_1/n$(No. 14)	$P\bar{1}$(No. 2)
a, Å	16.259(3)	10.970(2)
b, Å	21.627(4)	15.979(2)
c, Å	9.729(1)	9.670(3)
α, deg	90	102.51(1)
β, deg	105.15(1)	109.73(1)
γ, deg	90	88.36(1)
V, Å^3	3302(2)	1556(1)
Z	4	2
ρ(calcd), g cm^{-3}	1.181	1.31
Cryst dimens, mm	0.23×0.25×0.28	0.24×0.25×0.30
Temp., °C	−100	−100
Radiation	Mo-K_α (0.71069 Å from graphite monochromator)	
μ, cm^{-1}	7.10	7.592
2θ limits, deg	4–50	4–55
Total no. of unique observations	5813	7417
Data, $F_o^2 > 3\sigma(F_o^2)$	3576	4815
Final no. of variables	343	361
R	0.087	0.037
R_w	0.137	0.036

spectrum. One should also note the interaction between the benzoyl phenyl group and the nearby phenyl group of the chelate. The dihedral angle between these two groups is 16° and there is a marked bending at the *ipso* carbon atom which results in a displacement of P(1) of 0.32 Å from the phenyl plane.

Changing the nature of the ligands coordinated to the nickel center has a profound effect on the course of the resulting polymerization reactions [8]. Similarly, it has an effect on the course of reactions with carbon monoxide. The triphenylphosphine analog of **2**, complex **3**, can be prepared by the conventional technique, and its reaction with CO is analogous to that of **2**. If, instead of changing the ligand, L, the chelate ligand is changed, different behavior is observed. Complex **4** containing triethylphosphine and a new chelate ring reacts with excess CO in

(Continued on p. 151)



(**4**)

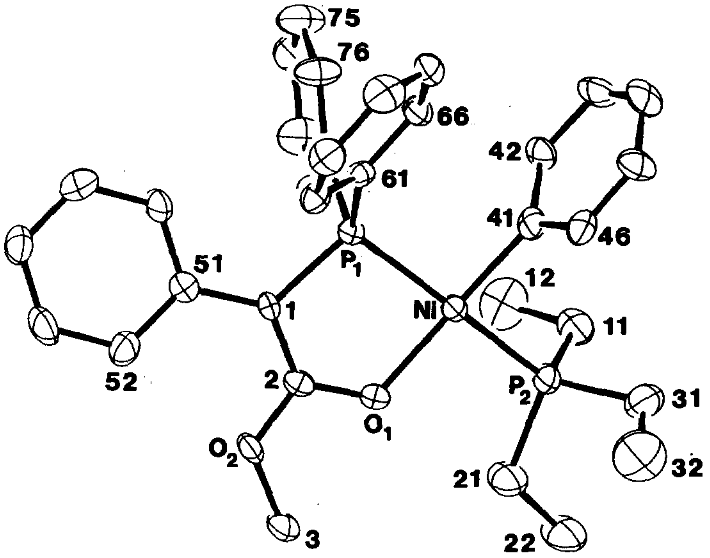


Fig. 1. Perspective view of $\mathrm{Ni(Ph_2PCPhC(OMe)O)(PEt_3)Ph}$ with atom labeling scheme. Hydrogen atoms are omitted for clarity.

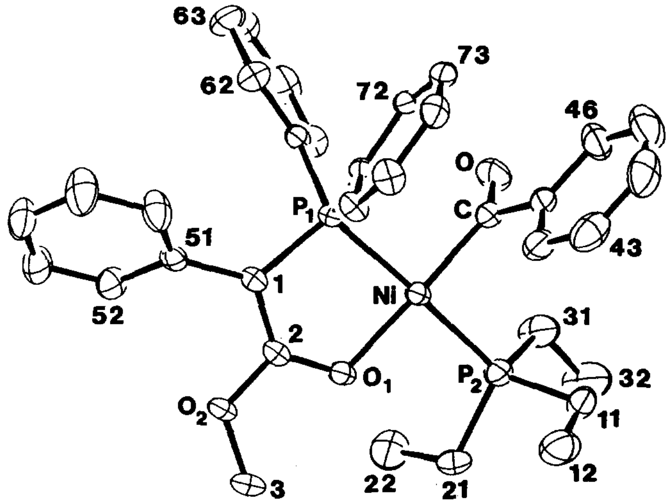


Fig. 2. Perspective view of $\mathrm{Ni(Ph_2PCPhC(OMe)O)(PEt_3)COPh}$ with atom labeling scheme. Hydrogen atoms are omitted for clarity.

Table 2

Positional and thermal parameters and their estimated standard deviations for $Ni(PPh_2C(Ph)C(OMe)O)(PEt_3)Ph$

Atom	x	y	z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Ni	0.0138(1)	0.30138(8)	0.4423(2)	0.00179(6)	0.00076(3)	0.0049(2)	0.0000(1)	0.0023(1)	0.0003(3)
P(1)	0.1068(2)	0.2350(2)	0.4034(4)	0.0017(1)	0.00083(7)	0.0047(4)	0.0000(2)	0.0022(3)	0.0003(3)
P(2)	−0.0577(2)	0.3707(2)	0.5266(4)	0.0026(1)	0.00092(8)	0.0070(4)	0.0006(2)	0.0043(4)	0.0007(3)
O(1)	−0.0250(5)	0.2343(4)	0.5374(9)	0.0020(4)	0.0011(2)	0.006(1)	0.0001(5)	0.0034(9)	0.0011(8)
O(2)	−0.0219(6)	0.1371(4)	0.6089(9)	0.0033(4)	0.0007(2)	0.009(1)	0.0003(5)	0.0063(10)	0.0016(8)
C(1)	0.0783(8)	0.1662(6)	0.484(1)	0.0019(5)	0.0006(3)	0.007(2)	0.0002(7)	0.003(1)	0.001(1)
C(2)	0.0111(8)	0.1800(6)	0.543(1)	0.0020(5)	0.0010(3)	0.004(1)	−0.0005(7)	0.002(1)	0.000(1)
C(3)	−0.0908(9)	0.1530(7)	0.670(1)	0.0034(6)	0.0013(3)	0.008(2)	0.0003(8)	0.007(2)	0.002(1)
C(11)	0.0118(10)	0.4291(7)	0.629(2)	0.0044(7)	0.0012(4)	0.009(2)	0.0003(8)	0.008(2)	−0.001(1)
C(12)	0.0844(12)	0.4047(9)	0.746(2)	0.0051(9)	0.0026(5)	0.011(2)	0.0004(12)	0.002(2)	−0.002(2)
C(21)	−0.1116(10)	0.3376(7)	0.652(2)	0.0046(7)	0.0015(4)	0.013(2)	0.0002(9)	0.010(2)	0.000(2)
C(22)	−0.1631(10)	0.3793(8)	0.718(2)	0.0062(7)	0.0017(4)	0.017(2)	0.0002(10)	0.017(2)	−0.001(2)
C(31)	−0.1381(9)	0.4141(8)	0.405(2)	0.0025(6)	0.0022(4)	0.010(2)	0.0008(9)	0.003(2)	0.001(2)
C(32)	−0.2104(12)	0.3785(10)	0.327(2)	0.0046(9)	0.0033(6)	0.015(3)	−0.0010(14)	0.000(3)	−0.001(2)
C(41)	0.0452(8)	0.3620(6)	0.329(1)	0.0027(5)	0.0009(3)	0.006(1)	0.0006(7)	0.003(1)	0.000(1)
C(42)	0.1204(9)	0.3973(6)	0.365(1)	0.0028(6)	0.0007(3)	0.008(2)	−0.0005(7)	0.003(2)	−0.001(1)
C(43)	0.1392(9)	0.4377(7)	0.266(2)	0.0034(6)	0.0011(3)	0.012(2)	−0.0016(8)	0.007(2)	−0.001(1)

C(44)	0.0854(10)	0.4439(7)	0.132(1)	0.0047(7)	0.0020(4)	0.006(2)	0.0009(10)	0.007(2)	0.004(1)
C(45)	0.0128(9)	0.4114(7)	0.097(1)	0.0028(6)	0.0017(4)	0.006(2)	−0.0007(8)	0.003(2)	0.001(1)
C(46)	−0.0080(9)	0.3710(7)	0.192(2)	0.0024(6)	0.0012(3)	0.009(2)	0.0010(8)	0.003(2)	0.000(1)
C(51)	0.1225(8)	0.1073(6)	0.493(1)	0.0020(5)	0.0010(3)	0.005(1)	−0.0003(7)	0.001(1)	0.000(1)
C(52)	0.0915(9)	0.0521(7)	0.537(2)	0.0019(6)	0.0013(3)	0.010(2)	0.0003(8)	0.001(2)	0.001(1)
C(53)	0.1368(10)	−0.0038(7)	0.542(2)	0.0035(7)	0.0008(3)	0.012(2)	−0.0006(8)	0.003(2)	0.002(1)
C(54)	0.2141(9)	−0.0067(7)	0.511(2)	0.0033(7)	0.0010(3)	0.009(2)	0.0011(8)	0.003(2)	0.000(1)
C(55)	0.2451(10)	0.0489(8)	0.468(2)	0.0031(6)	0.0022(4)	0.014(2)	0.0015(9)	0.008(2)	0.002(2)
C(56)	0.2005(9)	0.1039(7)	0.461(2)	0.0040(6)	0.0007(3)	0.014(2)	0.0009(8)	0.010(2)	0.001(1)
C(61)	0.1127(8)	0.2203(6)	0.221(1)	0.0015(5)	0.0011(3)	0.004(1)	0.0001(7)	0.001(1)	0.000(1)
C(62)	0.0845(8)	0.1647(6)	0.156(1)	0.0019(5)	0.0012(3)	0.005(2)	0.0003(7)	0.001(2)	0.000(1)
C(63)	0.0837(9)	0.1556(7)	0.012(2)	0.0027(6)	0.0012(3)	0.009(2)	−0.0004(8)	0.002(2)	−0.002(1)
C(64)	0.1094(9)	0.2018(8)	0.063(1)	0.0034(6)	0.0024(4)	0.004(1)	0.0004(10)	0.002(2)	0.000(2)
C(65)	0.1385(9)	0.2582(7)	0.003(1)	0.0029(6)	0.0012(3)	0.008(2)	0.0006(8)	0.004(2)	0.002(1)
C(66)	0.1385(9)	0.2671(6)	0.144(1)	0.0028(6)	0.0010(3)	0.007(2)	0.0002(8)	0.004(1)	0.001(1)
C(71)	0.2133(8)	0.2583(6)	0.503(1)	0.0017(5)	0.0008(3)	0.008(2)	−0.0002(7)	0.002(1)	0.001(1)
C(72)	0.2233(9)	0.2724(7)	0.649(1)	0.0020(5)	0.0023(4)	0.006(2)	−0.0003(9)	0.002(2)	0.001(1)
C(73)	0.3001(10)	0.2924(8)	0.734(2)	0.0029(6)	0.0028(5)	0.006(2)	−0.0010(10)	0.001(2)	0.000(2)
C(74)	0.3694(9)	0.2981(8)	0.679(2)	0.0020(6)	0.0021(4)	0.010(2)	−0.0006(9)	−0.001(2)	0.002(2)
C(75)	0.3618(9)	0.2833(8)	0.536(2)	0.0023(6)	0.0032(5)	0.008(2)	−0.0011(10)	0.003(2)	0.002(2)
C(76)	0.2838(9)	0.2642(8)	0.449(1)	0.0025(6)	0.0025(4)	0.006(2)	−0.0011(9)	0.004(2)	−0.001(2)

[a] The form of the anisotropic thermal parameter is: $\exp[-(B_{1,1}{}^{*}h^{*}h + B_{2,2}{}^{*}k^{*}k + B_{3,3}{}^{*}l^{*}l + B_{1,2}{}^{*}h^{*}k + B_{1,3}{}^{*}h^{*}l + B_{2,3}{}^{*}k^{*}l)]$.

Table 3

Positional and thermal parameters and their estimated standard deviations for $Ni(Ph_2PC(Ph)C(OMe)O)(PEt_3)(COPh)$ [a]

Atom	x	y	z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Ni	0.27839(3)	0.26198(2)	0.07922(4)	0.00349(2)	0.00146(2)	0.00627(3)	−0.00007(3)	0.00329(4)	0.00169(3)
P(1)	0.48372(6)	0.23169(4)	0.14419(7)	0.00348(5)	0.00137(2)	0.00529(6)	−0.00022(6)	0.00362(9)	0.00108(6)
P(2)	0.07349(6)	0.29292(5)	0.03285(8)	0.00394(6)	0.00208(3)	0.00848(8)	0.00045(7)	0.00363(10)	0.00211(8)
O	0.3404(2)	0.4347(1)	0.1488(2)	0.0080(2)	0.00184(7)	0.0097(2)	−0.0008(2)	0.0038(3)	0.0007(2)
O(1)	0.2475(2)	0.1481(1)	0.1036(2)	0.0037(1)	0.00167(7)	0.0098(2)	−0.0001(2)	0.0040(3)	0.0029(2)
O(2)	0.3236(2)	0.0274(1)	0.1781(2)	0.0050(2)	0.00174(7)	0.0104(2)	−0.0010(2)	0.0048(3)	0.0037(2)
C	0.3142(2)	0.3688(2)	0.0508(3)	0.0036(2)	0.00199(10)	0.0083(3)	0.0004(3)	0.0030(4)	0.0028(3)
C(1)	0.4751(2)	0.1296(2)	0.1829(3)	0.0045(2)	0.00134(9)	0.0059(3)	0.0001(2)	0.0049(3)	0.0012(2)
C(2)	0.3466(2)	0.1053(2)	0.1535(3)	0.0049(2)	0.00149(9)	0.0058(3)	−0.0003(2)	0.0044(4)	0.0013(3)
C(3)	0.1910(3)	−0.0004(2)	0.1350(3)	0.0055(2)	0.00255(11)	0.0129(4)	−0.0027(3)	0.0042(5)	0.0043(3)
C(11)	−0.0223(3)	0.2899(2)	−0.1624(3)	0.0047(2)	0.00406(13)	0.0103(3)	0.0013(3)	0.0024(5)	0.0061(3)
C(12)	−0.0356(3)	0.2009(2)	−0.2637(3)	0.0081(3)	0.00488(16)	0.0101(4)	−0.0028(4)	0.0018(6)	0.0025(4)
C(21)	−0.0184(2)	0.2208(2)	0.0888(3)	0.0041(2)	0.00321(12)	0.0106(3)	−0.0009(3)	0.0059(4)	0.0032(3)
C(22)	0.0328(3)	0..2245(2)	0.2575(3)	0.0075(3)	0.00506(16)	0.0113(3)	0.0020(4)	0.0104(4)	0.00052(4)
C(31)	0.0566(3)	0.4007(2)	0.1361(4)	0.0062(3)	0.00255(13)	0.0157(4)	0.0006(3)	0.0076(5)	0.0001(4)
C(32)	−0.0757(3)	0.4281(2)	0.1350(4)	0.0079(3)	0.00341(15)	0.0226(6)	0.0013(4)	0.0116(7)	−0.0008(5)
C(41)	0.3089(2)	0.3719(2)	−0.1064(3)	0.0035(2)	0.00257(10)	0.0091(3)	0.0009(3)	0.0040(4)	0.0046(3)
C(42)	0.2788(3)	0.2989(2)	−0.2206(3)	0.0051(2)	0.00367(13)	0.0081(3)	−0.0003(3)	0.0029(4)	0.0037(3)

C(43)	0.2738(3)	0.3035(2)	−0.3639(3)	0.0067(3)	0.00616(19)	0.0083(4)	0.0006(4)	0.0044(5)	0.0036(4)
C(44)	0.2990(3)	0.3813(2)	−0.3918(3)	0.0085(3)	0.00775(19)	0.0114(3)	0.0051(4)	0.0100(5)	0.0122(4)
C(45)	0.3319(3)	0.4538(2)	−0.2775(4)	0.0109(3)	0.00505(15)	0.0192(4)	0.0037(4)	0.0157(5)	0.0129(4)
C(46)	0.3371(3)	0.4495(2)	−0.1354(3)	0.0074(3)	0.00292(11)	0.0145(4)	0.0027(3)	0.0104(5)	0.0073(3)
C(51)	0.5873(2)	0.0817(2)	0.2558(3)	0.0046(2)	0.00132(9)	0.0066(3)	0.0001(2)	0.0038(4)	0.0009(3)
C(52)	0.5948(3)	0.0517(2)	0.3830(3)	0.0057(2)	0.00301(12)	0.0058(3)	0.0002(3)	0.0039(4)	0.0019(3)
C(53)	0.6976(3)	0.0065(2)	0.4528(3)	0.0078(3)	0.00412(14)	0.0072(3)	0.0011(4)	0.0027(5)	0.0052(3)
C(54)	0.7990(3)	−0.0095(2)	0.3987(3)	0.0074(3)	0.00398(14)	0.0118(4)	0.0044(3)	0.0049(5)	0.0066(4)
C(55)	0.7958(3)	0.0207(2)	0.2751(3)	0.0083(3)	0.00597(16)	0.0164(4)	0.0078(4)	0.0148(5)	0.0111(4)
C(56)	0.6920(3)	0.0656(2)	0.2043(3)	0.0080(3)	0.00423(13)	0.0118(3)	0.0048(3)	0.0121(4)	0.0087(3)
C(61)	0.5957(2)	0.3020(2)	0.3108(3)	0.0048(2)	0.00149(9)	0.050(2)	−0.0007(2)	0.0031(4)	0.0015(2)
C(62)	0.7293(3)	0.2997(2)	0.3472(3)	0.0048(2)	0.00273(11)	0.0071(3)	−0.0001(3)	0.0036(4)	0.0010(3)
C(63)	0.8102(3)	0.3516(2)	0.4789(3)	0.0053(3)	0.00395(14)	0.0081(4)	−0.0021(3)	−0.0011(5)	0.0021(4)
C(64)	0.7584(3)	0.4058(2)	0.5744(3)	0.0098(3)	0.00245(11)	0.0055(3)	−0.0024(3)	−0.0012(5)	0.0012(3)
C(65)	0.6263(3)	0.4089(2)	0.5392(3)	0.0105(3)	0.00208(11)	0.0055(3)	0.0012(3)	0.0053(5)	0.0012(3)
C(66)	0.5442(3)	0.3573(2)	0.4074(3)	0.0061(2)	0.00202(10)	0.0063(3)	0.0008(3)	0.0049(4)	0.0017(3)
C(71)	0.5524(2)	0.2293(2)	−0.0036(2)	0.0032(2)	0.00174(9)	0.0051(2)	0.0003(2)	0.0033(3)	0.0017(2)
C(72)	0.5990(2)	0.3058(2)	−0.0203(3)	0.0032(2)	0.00188(10)	0.0065(3)	−0.0002(2)	0.0025(4)	0.0014(3)
C(73)	0.6281(2)	0.3083(2)	−0.1482(3)	0.0041(2)	0.00270(11)	0.0074(3)	−0.0003(3)	0.0033(4)	0.0038(3)
C(74)	0.6148(3)	0.2348(2)	−0.2586(3)	0.0057(2)	0.00332(12)	0.0063(3)	0.0016(3)	0.0059(4)	0.0015(3)
C(75)	0.5708(3)	0.1584(2)	−0.2413(3)	0.0078(3)	0.00255(11)	0.0063(3)	0.0013(3)	0.0062(4)	0.0008(3)
C(76)	0.5379(2)	0.1558(2)	−0.1159(3)	0.0060(2)	0.00184(10)	0.0068(3)	0.0002(3)	0.0053(4)	0.0017(3)

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[a] The form of the anisotropic thermal parameter is: $\exp[-(B_{1,1}{}^{*}h^{*}h + B_{2,2}{}^{*}k^{*}k + B_{3,3}{}^{*}l^{*}l + B_{1,2}{}^{*}h^{*}k + B_{1,3}{}^{*}h^{*}k + B_{2,3}{}^{*}k^{*}l)]$.

Table 4

Selected bond distances (Å) and angles (°) in compounds **2** and **7**

	Compound **2**	Compound **7**
Distances		
Ni–P(1)	2.189(2)	2.195(1)
Ni–O(1)	1.914(4)	1.938(1)
Ni(P(2)	2.184(2)	2.202(1)
Ni–C(41)	1.867(6)	–
Ni–C	–	1.859(2)
C–C(4)	–	1.513(3)
C–O	–	1.221(3)
P(1)–C(1)	1.797(6)	1.763(2)
C(1)–C(2)	1.392(7)	1.390(3)
C(2)–O(2)	1.321(7)	1.363(2)
O(2)–C(3)	1.441(7)	1.426(3)
C(2)–O(1)	1.308(7)	1.276(3)
C(1)–C(51)	1.453(8)	1.481(3)
P(1)–C(61,71)	1.822(6)	1.820(2)
	1.826(6)	1.823(2)
C–C(arom)	1.34	1.373
	1.41(1)	1.399(4)
Angles		
P(1)–Ni–P(2)	167.1(1)	175.41(3)
P(1)–Ni–O(1)	85.2(1)	85.70(5)
P(1)–Ni–C(41)	93.0(2)	–
P(1)–Ni–C	–	92.02(7)
P(2)–Ni–O(1)	93.6(1)	92.78(5)
P(2)–Ni–C(41)	89.6(2)	–
P(2)–Ni–C	–	89.65(7)
O(1)–Ni–C(41)	173.1(2)	–
O(1)–Ni–C	–	176.94(9)
Ni–P(1)–C(1)	101.5(2)	100.49(8)
P(1)–C(1)–C(2)	108.7(5)	109.8(2)
P(1)–C(1)–C(51)	124.8(5)	125.6(2)
C(2)–C(1)–C(51)	126.4(6)	124.1(2)
Ni–C(1)–C(2)	119.9(4)	117.3(1)
O(1)–C(2)–C(1)	124.7(6)	126.5(2)
O(1)–C(2)–O(2)	114.5(5)	116.6(2)
C(1)–C(2)–O(2)	120.8(6)	116.9(2)
C(2)–O(2)–C(3)	119.5(5)	116.5(2)
Ni–C–C(41)	–	116.2(2)
Ni–C–O	–	124.6(2)
O–C–C(41)	–	119.3(2)
Ni–P(1)–C(61.71)	109.7(3)	113.41(7)
	119.7(3)	117.07(7)
Ni–P(2)–C(11,21,31)	111.6(2)	111.72(9)
	112.2(3)	113.48(8)
	118.8(3)	116.42(9)
Ni–C(41)–C(42,6)	117.6(5)	–
	126.0(5)	–
C(1)–C(51)–C(52,6)	120.2(6)	121.1(2)
	123.3(6)	122.6(2)

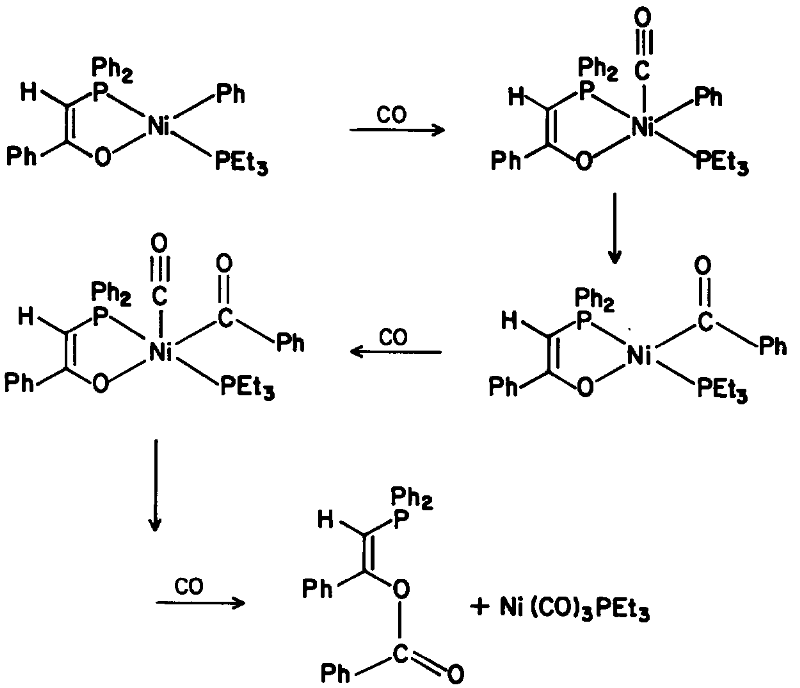

Fig. 3. Proposed mechanism for reaction of nickel complex with CO. The five-coordinate carbon monoxide complexes are not observed but the other species are.

toluene to give the expected benzoyl complex, but the reaction continues. The final products are $Ni(CO)_3(PEt_3)$ and the unusual ester, $Ph_2PCH{=}C(Ph)OCOPh$ (**8**), formed by the coupling of the chelate ring and the benzoyl group. Compound **8** is isolated by precipitation with hexane and recrystallization from toluene/hexane. The ^1H NMR spectrum shows only one ethylenic resonance as a doublet at 6.65 ppm with $J(PH))$ 1.1 Hz and absorptions consistent with four phenyl groups. The ^{31}P NMR spectrum of **8** consists of a single resonance at -26.63 ppm, and the infrared spectrum contains a strong ester band at 1730 cm^{-1}. These data are consistent with a single isomer which we believe is the *Z*-isomer arising from the *cis*-reductive elimination of the two groups. The isomer assignment is supported by alternate syntheses and NOE-difference NMR.

Complex **5** reacts in a manner similar to that of **4**, but the nickel(0) species obtained are slightly different. In this case, there is only a small quantity of the $Ni(CO)_3PPh_3$. The predominant species are dicarbonyls. Removal of solvent and recrystallization of the resulting solids from methylene chloride/ethanol yields a mixture of three $Ni(CO)_2L_x(PPh_3)_{2-x}$ where $x = 0, 1$, and 2. The second phosphine ligand, L, is again the ester **8**.

The temperature dependent ^{31}P NMR spectra of **2**, **3**, and **4** do not indicate phosphine dissociation. We believe that the mechanism of the reaction with CO is associative as shown in Fig. 3. Such a mechanism would be in accord with that proposed by Yamamoto for related CO reactions with nickel aryl and alkyl species.

The gross features of both ethylene homopolymerization and ethylene/CO copolymerization can be divided into three separate steps: initiation, propagation,

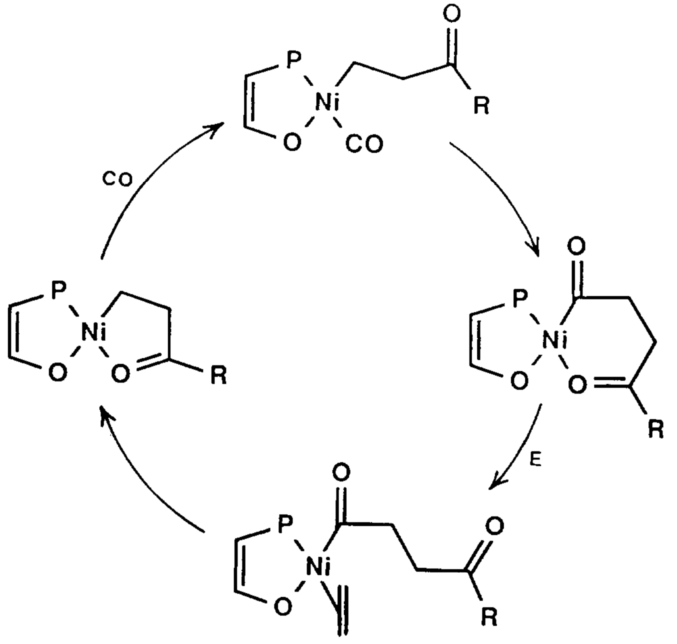

Fig. 4. Proposed mechanism for the alternating copolymerization of ethylene with CO.

and termination. There are features common to both systems, but the details of the energetics of the various species on the catalytic cycles play a crucial role. In the ethylene homopolymerization, the limiting step in initiation is insertion of ethylene into the relatively stable Ni–phenyl bond. Once this occurs, propagation begins or β-hydride elimination liberates styrene and the resulting nickel hydride initiates polymerization. Insertion into a preformed Ni-methyl bond is much easier so propagation is initiated at a lower temperature. Attempted initiation of polymerization in the presence of CO takes the chemistry off in a different direction. Insertion of CO into the Ni–phenyl bond to yield a benzoylnickel compound is more facile than insertion of ethylene, and the resulting benzoyl compound is more stable than the phenyl compound. Once the benzoyl species is formed, ethylene insertion becomes impossible and no polymerization occurs. If, on the other hand, the phenyl group has already been removed by ethylene homopolymerization, then CO inserts into a Ni–alkyl bond yielding a acylnickel. The fact that copolymer is obtained demonstrates that ethylene is able to insert into a nickel–acyl bond. We presume that copolymerization proceeds as indicated in Fig. 4. One of the acyl species is probably the resting state of the catalyst with ethylene insertion being the rate limiting step. We expect that CO insertion into the $NiCH_2CH_2COR$ species would be facile. It is likely that chelation by the β-carbonyl of the propagating chain contributes to the stability of the ethylene insertion product [15*].

Catalyst decomposition in the ethylene homopolymerization systems usually occurs by disproportionation of the nickel species to divalent $Ni(chelate)_2$ and

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* This and other references marked with asterisks indicate notes occurring in the list of references.

unknown nickel(0) species. In the ethylene/CO copolymerization system, zerovalent nickel carbonyl species are readily available thermodynamic sinks for the active catalyst. Thus, reductive elimination of the chelate ligand and the benzoyl, or presumably acyls in actively propagating systems, yield the nickel(0) species observed.

Experimental

Many of the compounds are moderately moisture- or air-sensitive materials and were handled in the prepurified nitrogen atmosphere of a Vacuum Atmospheres drybox. Operations outside the drybox were carried out using standard Schlenk techniques [16]. Solvents were dried by standard techniques [16]. Di(1,5-cyclooctadiene)nickel was prepared by the method of Schunn [17]. The phosphorus ylids were prepared by literature methods [18] or are commercially available.

NMR spectra were recorded on Bruker HFX-90, Nicolet NT-300 or Nicolet NT-360 spectrometers. The 600 MHz spectra were recorded at Carnegie-Mellon University at 140.96 kG.

Preparation of **2**. To a solution of **1** (2.1 g) and 0.65 g of PEt_3 in 100 ml of toluene was added 1.37 g of $Ni(COD)_2$. The honey-brown solution was stripped on a vacuum line to give an oil which upon addition of 100 ml hexane yielded yellow crystals. The product was collected, washed with hexane, and dried under N_2. Yield 2.75 g (94%). The crystal structure determination is reported below. Anal. Found: C, 69.42; H, 6.69; O, 4.88. **1** · 1/2 $C_7H_8C_{36.5}H_{42}NiO_2P_2$ (639.41) calcd.: C, 69.50; H, 6.62; O, 5.00%. $^{31}P\{^1H\}$ NMR: *AB* spin system, *A* 15.84 ppm, *B* 14.13 ppm, *J* 276 Hz.

Preparation of **3**. 2.80 g of $Ni(COD)_2$ was added to 75 ml toluene which contained 4.3 g of $Ph_3P{=}CPhCO_2CH_3$ and 2.8 g of PPh_3. The resulting dark red solution was stirred overnight. The solvent was stripped on a vacuum line. The residue was slurried in hexane and filtered to give a yellow powder (7.5 g). Recrystallization from toluene/hexane gave a deep yellow crystalline solid. Anal. Found: C, 73.70; H, 5.16. $C_{45}H_{38}NiO_2P_2$ (731.36) calcd.: C, 73.90; H, 5.24%. $^{31}P\{^1H\}$ NMR: *AB* spin system, *A* 25.67 ppm, *B* 21.16 ppm, *J* 273.6 Hz.

Preparation of **4**. In the drybox, 7.6 g of $Ph_3P{=}CHCOPh$, 5.5 g of $Ni(COD)_2$, and 2.4 g of PEt_3 were allowed to react in 150 ml of toluene. After stirring overnight, the mixture was filtered and stripped to dryness on a vacuum line. The resulting solids were slurried in hexane and collected by vacuum filtration. The microcrystalline yellow product (10.8 g) was dried under vacuum. $^{31}P\{^1H\}$ NMR: *AB* spin system, *A* 21.22 ppm, *B* 17.99 ppm, *J* 286.5 Hz.

Complex **5** was prepared analogously. $^{31}P\{^1H\}$ NMR: *A* 25.76 ppm, *B* 24.10 ppm, *J* 284.5 Hz.

Reaction of **2** *with CO*. A solution of 2.7 g of **2** in 50 ml toluene was allowed to react with 50 psig of carbon monoxide. The orange solution darkened slightly. Stirring was continued overnight. Most of the solvent was removed under vacuum giving a dark yellow oil. On addition of hexane, a yellow powder formed and was isolated by vacuum filtration. The compound was recrystallized by dissolving in a minimum amount of toluene, filtering, and then adding 60 ml of hexane. At −20 ° C, crystals of **7** formed. They were collected, washed with hexane, and dried at room temperature under vacuum. The crystal structure determination is reported below. Anal. Found: C, 66.83; H, 6.36; O, 7.58. $C_{34}H_{38}NiO_3P_2$ (615.34) calcd.: C, 66.37; H, 6.22; O, 7.80%. $^{31}P\{^1H\}$ NMR: *AB* spin system, *A* 19.23 ppm, *B* 17.65 ppm, *J* 198.9 Hz.

Reaction of 4 with CO. A 10 ml toluene solution containing 2.40 g of **4** was pressurized to 50 psig with carbon monoxide and stirred for 2 h. After relieving the pressure and purging with nitrogen, the solvent was removed under reduced pressure and the light yellow oil extracted with hexane to give a white solid which was dissolved in a minimum amount of toluene. Addition of an equal amount of hexane and allowing the solution to stand at −25 °C yielded a white solid, identified as **8**, which was collected, washed with hexane, dried at 0.1 mmHg 20 °C for 2 h. M.p.: 118–120 °C. Anal. Found: C, 79.2; H, 5.18; O, 7.56. $C_{27}H_{21}O_2P$ calcd.: C, 79.4; H, 5.18; O, 7.83%. The ^1H NMR spectrum in benzene-d_6 showed a doublet =CH proton at 6.65 ppm, *J*(PH) 1.7 Hz and the phenyl protons as multiplets centered at 7.0, 7.5, and 8.1 ppm. The IR spectrum (Nujol mull) showed CO_2R absorption at 1730 cm^{-1}.

Reaction of 5 with CO. A solution 2.0 g of **5** in 100 ml toluene was stirred for 45 min under 20 psig CO. After releasing the pressure, 100 ml hexane was added and the pale yellow solution was stored at −20 °C for 18 h. The solvent was removed under reduced pressure and the resulting pale yellow solid was dissolved in 75 ml of methylene chloride to which ethanol (50 ml) was added. Reducing the solvent volume yielded 1.8 g (93%) pale yellow crystals in two crops. The crystals were washed with ethanol and ether and dried in vacuo. $^{31}P\{^1H\}$ NMR analysis indicated that the isolated material was a mixture of $Ni(CO)_2L_x(PPh_3)_{2-x}$ ($x = 0, 1, 2$) where L is **8**.

Confirmation of structure of 8. As an alternative synthesis of the ester **8**, the thallium salt **6**, was treated with benzoyl chloride to give the identical compound. Phosphorus NMR indicated that only a single isomer was obtained from this synthesis and that it was identical with that obtained by reductive elimination from the nickel complex. The *ortho* protons on the phosphine phenyls and the vinylic phenyl show strong Nuclear Overhauser Enhancement from the vinylic proton while the benzoic phenyl does not [19]. If the *E*-isomer had been obtained, the vinylic phenyl would not be expected to show enhancement and the benzoic phenyl might show some enhancement.

X-Ray data collection and structure solutions and refinements

Crystals of compound **2** were grown from toluene/hexane by cooling to −30 °C. A suitable crystal was encapsulated in a glass capillary under an atmosphere of N_2. The crystal was then placed on a Syntex P3 diffractometer and cooled to −100 °C. After the cell and space group had been determined (see Table 1), the unit cell parameters were refined on the basis of 50 computer-centered reflections.

The ω-scan technique was used for collecting the intensity data (variable scan rate, 3.0–10.0° min^{-1}, 1.0° range). Four standard reflections were chosen, and their intensities were remeasured every 200 reflections; no significant deviations in these standard intensities were observed. Empirical corrections for absorption were derived from the intensities of several reflections measured every 10° about the diffractor vector. The data were processed by using counting statistics and a ρ value of 0.02 to derive standard deviations [20].

The solution and refinement of the structure were carried out by using local modifications of programs supplied by the Enraf–Nonius Corp. [21]. The structure was solved and refined by the usual combination of Patterson and Fourier syntheses and full matrix least-squares refinements. In the least-squares refinements, the function minimized was $\Sigma\omega(|F_o|-|F_c|)^2$, where $|F_o|$ and $|F_c|$ are, respectively, the observed and calculated structure amplitudes and where $\omega = 1/\sigma^2(F_o)$. The atomic scattering factors and anomalous dispersion terms were taken from the standard compilations [22]. Hydrogen atoms were located, placed in idealized positions, and included as fixed contributions in the final cycles of refinement. The hemi-toluene of solvation was badly disordered about the center of inversion. No chemically reasonable model could be defined, but the *R* factor decreased to less than 0.05 when C atoms were placed in this vicinity. These were not included in the final refinement.

The positional and isotropic thermal parameters for the atoms are listed in Table 2, with tables of anisotropic thermal parameters and hydrogen atom positions available directly from the authors, as are observed and calculated structure factor amplitudes. Final values for the agreement indices are in Table 1. The four highest peaks in the final difference-Fourier map were 0.78 to 3.8 e $Å^{-3}$ near the center of inversion. All other peaks were less than 0.6 e $Å^{-3}$.

Crystals of complex **7** were grown similarly. Data collection and processing and structure solution and refinement were carried out in a manner analogous to that above, except that the variable scan rate was 4.0–10.0° min^{-1} over a 1.0° range. Crystallographic data are included in Table 1. Positional and isotropic thermal parameters of the atoms of compound **7** are listed in Table 3. Anisotropic thermal parameters and hydrogen atom positions are available as supplementary material from the authors, as is a listing of observed and calculated structure factor amplitudes. The agreement indices are listed in Table 1. The highest peaks in a final difference-Fourier were less than 0.4 e $Å^{-3}$.

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