Inorg. Chem. 1995, 34, 1288−1291

Synthesis and Molecular Structure of a Nickel(II) Complex Containing a Pyrazolone-Derived Phosphane Ligand: $[Ni(\eta^5\text{-}C_5Ph_5)\{Ph_2\overline{PC{=}C(O)N(Ph)N{=}C}(Me)\}]$

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Received April 29, 1994

Introduction

In recent years, there has been a great deal of interest shown in the study of nickel(II) complexes containing three-electron chelating ligands of the type $[Ph_2PCH{=}C(R)O]^-$.[1] Complexes containing such ligands not only serve as precursors for the oligomerization of olefins[1fg,2] but also give access to soluble matrix polyacetylenes.[3] We recently described a general synthetic route to η^5-pentaphenylcyclopentadienyl complexes of type **1** (see Scheme 1), which were shown to behave as effective catalysts for low-pressure oligomerization of ethene in the presence of sodium borohydride.[4] This latter additive is believed to generate a nickel hydrido species allowing the initial insertion of an ethene molecule. The methodology used for the preparation of these catalyst precursors is based on the use of β-(carbonyl)phosphanes and circumvents the disadvantages of the so-called "ylide" route.[5] Furthermore, it opens interesting possibilities for the preparation of a large variety of new nickel oligomerization catalysts containing dissymmetric chelates. As a further illustration of our synthetic principle, we report here the synthesis, molecular structure, and catalytic activity of a (pentaphenylcyclopentadienyl)nickel(II) complex containing a chelating pyrazolone-derived phosphane ligand. This study will provide some information on the effect of a strongly electron withdrawing pyrazole ring fused to a *P,O* metallacycle on the catalytic properties of a nickel complex designed for ethene polymerization.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using standard Schlenk-tube techniques. Solvents including $CDCl_3$ were dried over suitable reagents and were freshly distilled under argon before use. The IR spectra were recorded on a IFS 25 Bruker spectrometer. The ^1H NMR data were referenced relative to residual protiated solvents (7.25 ppm for $CDCl_3$); the ^{13}C NMR chemicals shifts are reported relative to $CDCl_3$ (77.0 ppm), and the ^{31}P NMR data are given relative to external 85% H_3PO_4 in H_2O. The mass spectrum of compound **3** was recorded on a ZAB HF VG Analytical using *m*-nitrobenzyl alcohol as matrix. The complex $[NiBr(\eta^5\text{-}C_5Ph_5)(CO)]$[6] and the phosphane salt $Na[Ph_2\overline{PC{=}C(O)N(Ph)N{=}C}(Me)]$[7] were prepared according to published procedures. Elemental analyses were performed by the Service de Microanalyse du CNRS de l'Université Louis Pasteur. The catalytic runs were performed in a 100 mL glass-lined stainless steel autoclave containing a magnetic stirring bar. In a typical run, a given quantity of the catalyst precursor was introduced under argon into the autoclave. After two argon-vacuum cycles, the solvent was added (20 mL). Then a THF solution with $NaBH_4$ was introduced. The autoclave was pressurized with ethene and heated to 90 °C. The stirring speed was 600 rpm. At the end of the catalytic run, the autoclave was cooled and then slowly opened. The liquid phase was analyzed by GC. The solid (polyethene) was filtered off, washed with toluene, and dried in vacuo.

Preparation of $[Ni(\eta^5\text{-}C_5Ph_5)\{Ph_2\overline{PC{=}C(O)N(Ph)N{=}C}(Me)\}]$ (3). To a solution of $[Ni(\eta^5\text{-}C_5Ph_5)Br(CO)]$ (0.612 g, 1.00 mmol) in CH_2Cl_2 (30 mL) was added $Na[Ph_2\overline{PC{=}C(O)N(Ph)N{=}C}(Me)]$ (**2**) as powder (0.358 g, 1.00 mmol). The solution instantly turned dark red. After 1 h of stirring, the solvent was evaporated to dryness. The residue was treated with toluene (30 mL), and the resulting mixture was stirred for a further 30 min. After filtration through a small silica gel column, the solvent was removed in vacuo. Recrystallization from CH_2Cl_2−pentane gave **3** (70%) as dark-red crystals. Mp: >210 °C. IR (KBr): 1599 (m), 1587 (m), 1537 (s), 1504 (s), 1481 (m), 1456 (m), 1443 (m), 1437 (sh), 1433 (sh), 1424 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.56−6.83 (40 H, aromatic H), 1.78 (s, 3H, Me of pyrazole ring). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.1 (s). ^{13}C NMR ($CDCl_3$): δ 172.49 (d, CO, $^2J(PC) \approx 28$ Hz), 147.49 (s, *C*(Me)=N), 139.24−118.33 (aromatic C's), 109.23 (s, C's of C_5 ring), 91.18 (d, PC(pyrazole), $J(PC) = 70$ Hz), 14.55 (s, Me). MS (FAB MS): *m/e* 861 (M + H$^+$, 100%). Anal. Calcd for $C_{57}H_{43}N_2NiOP$ (M_r = 861.66): C, 79.45; H, 5.03; N, 3.25. Found: C, 79.27; H, 5.27; N, 3.26.

Catalytic Run with Complex 3. A solution of $NaBH_4$ (0.0015 g, 0.040 mmol) in THF (3 mL) was introduced into a 100 mL autoclave containing a solution of **3** (0.0180 g, 0.020 mmol) in toluene (20 mL). The reactor was pressurized with ethene (6.60 g, 203.18 mmol, 28 bar at 25 °C) and the temperature raised to 90 °C (initial pressure at this temperature: ca. 38 bar). After 4.5 h, the autoclave was cooled to room temperature. At this stage, the ethene conversion was 86%. The content was analyzed by GC. The GC analysis of the liquid phase

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Scheme 1

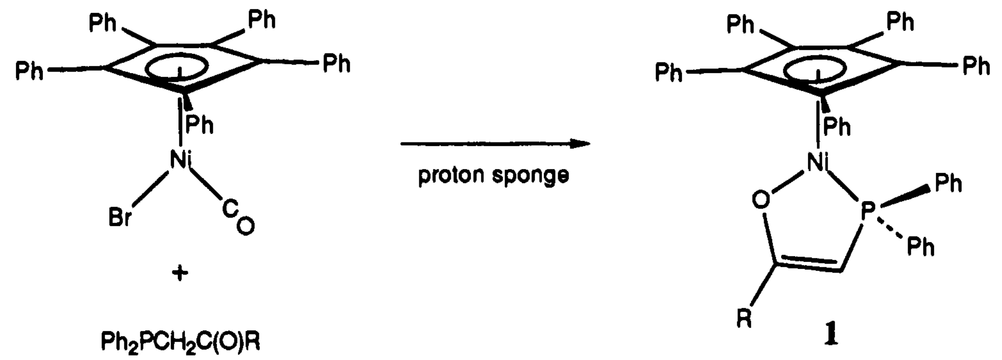

Table 1. Crystallographic Data for $[Ni(\eta^5\text{-}C_5Ph_5)\{Ph_2PC{=}C(O)N(Ph)N{=}C(Me)\}]$ (3)

formula	$C_{57}H_{43}N_2NiOP$	T, K	293
fw	861.66	λ, Å	0.710 73
a, Å	11.309(7)	space group	$P\bar{1}$
b, Å	17.32(1)	Z	4
c, Å	23.99(1)	D(calcd), g cm^{-3}	1.270
α, deg	79.90(5)	μ, cm^{-1}	5.07
β, deg	76.87(5)	θ range, deg	3–30
γ, deg	88.91(5)	R^a	0.077
V, Å^3	4505(6)	$R_w{}^b$	0.083

$^a R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(F_o)$.

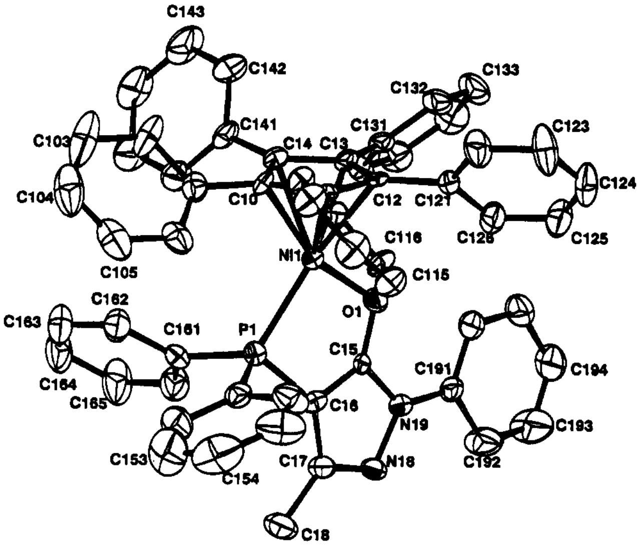

Figure 1. 1 Molecular structure of **3a**, showing the atom-numbering scheme. Thermal ellipsoids are drawn at 30% probability.

and of the mixture obtained after hydrogenation with Pd/C revealed mainly the presence of linear olefins (C_4–C_{34}) of which ca. 87% are α-olefins. The amount of branched isomers was ca. 3%. The amount of insoluble polyethene was 0.500 g (8.5%).

Crystal Structure Determination for 3. Suitable single crystals of **3** were obtained by slow diffusion of pentane into a solution of **3** in dichloromethane. A crystal of approximate size 0.70 × 0.70 × 0.60 mm was studied on a CAD4 ENRAF-NONIUS diffractometer with graphite-monochromatized Mo Kα radiation. Crystal data and parameters of data collection and structure refinement are compiled in Table 1. The asymmetric unit contains two crystallographically independent molecules. An attempted reduction of the triclinic to a C-centered monoclinic unit cell resulted in both unacceptable metric parameters and unsatisfactory internal agreement factors for reflections averaged in the 2/*m* Laue class. Structure solution and refinement was achieved with the local version of the SDP program system.[8] The Ni and P atoms were located by direct methods; the remaining atom positions resulted from subsequent cycles of refinement and difference Fourier syntheses. No high correlations between the two independent molecules were encountered. After convergence of the isotropic refinement, an empirical absorption correction with the program DIFABS[9] was applied to the original data set, and averaging of symmetry-related reflections was repeated. In the final least-squares full-matrix refinement, on the basis of 9664 observed independent reflections for 1118 variables, anisotropic displacement parameters for all non-hydrogen atoms were refined, H atoms were included in structure factor calculations, and a correction for secondary extinction ($E = 2.2 \times 10^{-7}$) was applied to F_c. Convergence results are compiled in Table 1. A final difference Fourier synthesis showed a local residual maximum of 1.3 e Å^{-3} at 1.0 Å from Ni1.

Results and Discussion

Upon treatment of a dichloromethane solution of $[Ni(\eta^5\text{-}C_5Ph_5)Br(CO)]$ with the sodium phosphinopyrazololate **2**, the air-stable dark-red complex **3** was formed in ca. 70% isolated yield (eq 1). This reaction is basically similar to that represented in Scheme 1. The ^{31}P NMR spectrum of **3** displays a signal at −5.1 ppm (free ligand δ −34.5), which appears rather high-field-shifted when compared with the signals of other previously

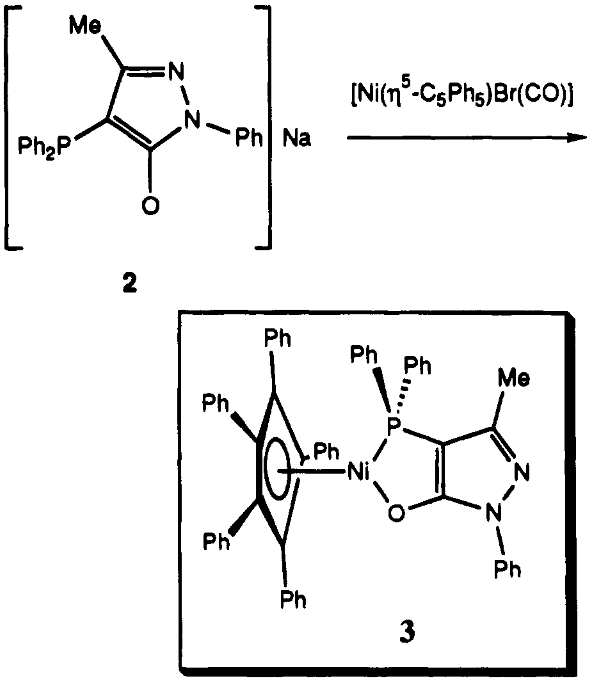

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for **3a** and **3b**

atom	x	y	z	B(eq),[a] Å^2	atom	x	y	z	B(eq),[a] Å^2
Molecule **3a**									
Ni	0.07778(7)	0.30520(5)	0.24329(4)	2.17(2)	C126	−0.0036 (6)	0.3389 (5)	0.3955(3)	3.8(2)
P1	0.0117(1)	0.3514(1)	0.16445(7)	2.40(4)	C131	0.0756(5)	0.1717(4)	0.3526(3)	2.4(1)
O1	−0.0869 (3)	0.2910(3)	0.2878(2)	3.0(1)	C132	0.0818(6)	0.1630(4)	0.4098 (3)	3.5(2)
N18	−0.3452(4)	0.3464(3)	0.2348 (2)	2.9(1)	C133	0.0066(8)	0.1090(5)	0.4530(3)	4.5(2)
N19	−0.2888(4)	0.3140(3)	0.2787(2)	2.5(1)	C134	−0.0742(7)	0.0626(5)	0.4366(4)	4.7(2)
C10	0.2661(5)	0.2949 (4)	0.2229 (3)	2.4(1)	C135	−0.0799 (7)	0.0700(5)	0.3794(3)	4.0(2)
C11	0.2413(5)	0.3520(4)	0.2624(3)	2.1(1)	C136	−0.0054(6)	0.1235(4)	0.3378(3)	3.1(2)
C12	0.1679(5)	0.3123(4)	0.3139 (3)	2.1(1)	C141	0.2301(6)	0.1440(4)	0.2311(3)	2.8(2)
C13	0.1486(5)	0.2329(4)	0.3080(3)	2.1(1)	C142	0.1916(7)	0.1318(4)	0.1835(3)	4.0(2)
C14	0.2153(5)	0.2193(4)	0.2525(3)	2.6(2)	C143	0.2056(8)	0.0608(5)	0.1653(4)	5.4(2)
C15	−0.1638(5)	0.3168(4)	0.2566(2)	1.9(1)	C144	0.2573(8)	0.0003(5)	0.1944(4)	5.8(3)
C16	−0.1422(5)	0.3535(4)	0.2009(3)	2.5(1)	C145	0.2974(9)	0.0109 (5)	0.2434 (4)	6.2(3)
C17	−0.2577(5)	0.3699(4)	0.1882(3)	2.8(2)	C146	0.2841(7)	0.0825(5)	0.2617(4)	4.4(2)
C18	−0.2857(6)	0.4074 (5)	0.1329 (3)	4.7(2)	C151	0.0586(5)	0.4480(4)	0.1231(3)	3.0(2)
C101	0.3502(5)	0.3107(4)	0.632(3)	3.0(2)	C152	0.0617(7)	0.5081(5)	0.1539(4)	4.5(2)
C102	0.4354(6)	0.2558(5)	0.1474(4)	4.9(2)	C153	0.1018(8)	0.5825(5)	0.1255(5)	6.5(3)
C103	0.5140(8)	0.2692(6)	0.0918(4)	7.3(3)	C154	0.1348(8)	0.5979(6)	0.0645(5)	7.4(3)
C104	0.5092 (7)	0.3379 (6)	0.0549 (4)	6.8(3)	C155	0.129(1)	0.5405 (6)	0.0355(4)	7.9(3)
C105	0.4271(7)	0.3923(6)	0.0700(4)	5.8(2)	C156	0.0899(8)	0.4659(5)	0.0629 (4)	5.1(2)
C106	0.3478(6)	0.3794(5)	0.1242 (3)	4.0(2)	C161	0.0199(6)	0.2888(4)	0.1117(3)	2.8(2)
C111	0.2831(5)	0.4352(4)	0.2507 (3)	2.3(1)	C162	0.1300(6)	0.2762(5)	0.0725 (3)	3.9(2)
C112	0.4063(6)	0.4530(4)	0.2257(3)	3.1(2)	C163	0.1342 (7)	0.2238 (5)	0.0359 (4)	5.1(2)
C113	0.4465 (6)	0.5313(4)	0.2140(3)	3.9(2)	C164	0.0338(8)	0.1781(6)	0.0366(4)	5.6(2)
C114	0.3691(7)	0.5897 (5)	0.2268(4)	4.6(2)	C165	−0.0740(7)	0.1898(6)	0.0746 (4)	6.1(2)
C115	0.2462(7)	0.5725(4)	0.2534(3)	3.8(2)	C166	−0.0805 (6)	0.2426(5)	0.1114(3)	4.2(2)
C116	0.2048(6)	0.4944(4)	0.2642 (3)	3.1(2)	C191	−0.3584(5)	0.2741(4)	0.3319(3)	2.7(2)
C121	0.1195(5)	0.3460(4)	0.3670(3)	2.5(1)	C192	−0.4841(6)	0.2829 (6)	0.3438 (4)	5.4(2)
C122	0.1961(7)	0.3845 (5)	0.3916(3)	4.3(2)	C193	−0.5534(7)	0.2417(6)	0.3952 (4)	7.1(3)
C123	0.1511(8)	0.4132(5)	0.4421(4)	5.9(2)	C194	−0.5028(7)	0.1969(5)	0.4345(4)	4.9(2)
C124	0.0307(8)	0.4055(5)	0.4694(3)	5.0(2)	C195	−0.3802(7)	0.1880(5)	0.4230(3)	4.2(2)
C125	−0.0458(7)	0.3679 (5)	0.4454(4)	4.8(2)	C196	−0.3090(6)	0.2291(4)	0.3722(3)	3.2(2)
Molecule **3b**									
Ni2	0.55680(7)	0.79717(5)	0.26462(4)	2.24(2)	C226	0.5840(7)	0.9544(5)	0.1452(4)	4.6(2)
P2	0.4184(2)	0.7777(1)	0.34761(8)	2.54(4)	C231	0.7036(5)	0.7140(4)	0.1546(3)	2.5(1)
O2	0.4311(4)	0.8042(3)	0.2220(2)	2.8(1)	C232	0.6116(6)	0.7205(5)	0.1262(3)	3.7(2)
N28	0.1224(5)	0.7556(4)	0.2855(3)	3.9(2)	C233	0.6058(7)	0.6754(5)	0.0842(3)	4.5(2)
N29	0.2171(4)	0.7801(3)	0.2387(3)	3.0(1)	C234	0.6993(7)	0.6245(5)	0.0691(3)	4.4(2)
C20	0.7266(5)	0.8032(4)	0.2842(3)	2.8(2)	C235	0.7933(7)	0.6190(5)	0.0969(4)	4.5(2)
C21	0.7139(5)	0.8728(4)	0.2417(3)	2.4(1)	C236	0.7977(6)	0.6629(4)	0.1385(3)	3.7(2)
C22	0.6961(5)	0.8483(4)	0.1926(3)	2.4(1)	C241	0.7564(5)	0.6542(4)	0.2779(3)	2.6(1)
C23	0.7078(5)	0.7622(4)	0.1999(3)	2.2(1)	C242	0.8603(6)	0.6364(4)	0.2996(3)	3.3(2)
C24	0.7307(5)	0.7368(4)	0.2539(3)	2.2(1)	C243	0.8833(7)	0.5608(5)	0.3212(4)	4.6(2)
C25	0.3221(5)	0.7871(4)	0.2580(3)	2.5(1)	C244	0.8061(8)	0.4996(5)	0.3219(4)	5.6(2)
C26	0.2966(5)	0.7675(4)	0.3154(3)	3.2(2)	C245	0.7037(8)	0.5168(5)	0.3009(4)	5.1(2)
C27	0.1673(6)	0.7487(5)	0.3320(3)	3.8(2)	C246	0.6779(6)	0.5919(4)	0.2795(3)	3.6(2)
C28	0.0947(7)	0.7179(6)	0.3913(4)	6.3(3)	C251	0.3901(6)	0.8610(4)	0.3852(3)	3.1(2)
C201	0.7514(5)	0.8002(4)	0.3421(3)	2.3(1)	C252	0.2842(7)	0.9029(5)	0.3861(4)	4.4(2)
C202	0.7081(6)	0.7390(4)	0.3861(3)	3.1(2)	C253	0.2680(9)	0.9702(5)	0.4088(4)	6.3(3)
C203	0.7304(6)	0.7354(5)	0.4405(3)	4.3(2)	C254	0.3540(9)	0.9973(5)	0.4329(4)	5.9(3)
C204	0.8019(8)	0.7948(6)	0.4507(3)	5.4(2)	C255	0.4583(8)	0.9566(5)	0.4322(4)	5.6(2)
C205	0.8462(7)	0.8544(5)	0.4069(3)	5.0(2)	C256	0.4798(7)	0.8882(5)	0.4097(3)	4.0(2)
C206	0.8229(6)	0.8585(4)	0.3522(3)	3.6(2)	C261	0.4104(5)	0.6933(4)	0.4045(3)	3.1(2)
C211	0.7257(6)	0.9556(4)	0.2475(3)	2.7(2)	C262	0.3967(7)	0.6970(5)	0.4622(3)	4.4(2)
C212	0.8326(7)	0.9977(5)	0.2190(4)	4.2(2)	C263	0.3838(8)	0.6295(6)	0.5033(4)	5.7(3)
C213	0.8445(7)	1.0755(5)	0.2219(4)	5.1(2)	C264	0.3865(8)	0.5588(6)	0.4882(4)	6.2(3)
C214	0.7520(9)	1.1137(5)	0.2524(4)	6.1(3)	C265	0.4021(8)	0.5530(5)	0.4313(5)	6.2(3)
C215	0.6465(8)	1.0729(5)	0.2819(4)	6.4(3)	C266	0.4129(7)	0.6190(5)	0.3884(4)	4.8(2)
C216	0.6338(7)	0.9949(4)	0.2788(4)	4.1(2)	C291	0.1955(6)	0.7940(4)	0.1823(3)	3.4(2)
C221	0.6730(6)	0.9001(4)	0.1402(3)	2.8(2)	C292	0.2887(7)	0.8019(6)	0.1344(3)	4.9(2)
C222	0.7447(8)	0.8960(5)	0.0857(4)	5.3(2)	C293	0.2653(8)	0.8184(7)	0.0802(4)	6.8(3)
C223	0.727(1)	0.9466(7)	0.0373(4)	8.5(3)	C294	0.150(1)	0.8251(8)	0.0736(5)	9.5(4)
C224	0.636(1)	0.9997(7)	0.0419(4)	7.6(3)	C295	0.0567(9)	0.816(1)	0.1224(5)	12.2(5)
C225	0.5636(8)	1.0031(6)	0.0962(4)	6.5(3)	C296	0.0781(7)	0.8016(7)	0.1772(4)	8.2(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

described nickel(II) complexes containing three-electron *P,O* chelating systems.[3-5] This value is consistent with the electron-withdrawing character of pyrazolone ring systems which is higher than that of a CF_3 group.[10] In the ^{13}C NMR spectrum, the P*C* carbon atom of the metallacycle appears as a doublet at 91.18 ppm with J(PC) = 70 Hz. Characteristic IR data are given in the Experimental Section.

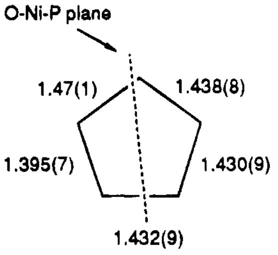
The structure of complex **3** was elucidated by an X-ray diffraction study. Crystal data are given in Table 1, and fractional positional parameters in Table 2.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **3**[a]

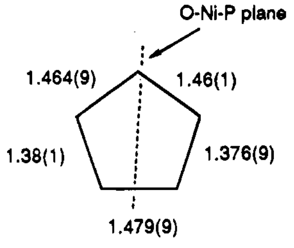
	Molecule **3a**		
P1–C16	1.764(6)	Ni1–C10	2.086(6)
P1–C151	1.811(7)	Ni1–C11	2.205(6)
P1–C161	1.792(8)	Ni1–C12	2.188(7)
C16–C17	1.419(9)	Ni1–C13	2.112(6)
C17–N18	1.321(7)	Ni1–C14	2.153(6)
N18–N19	1.385(8)		
N19–C15	1.391(7)		
	P1–Ni1–O1	90.0(1)	
	Molecule **3b**		
P2–C26	1.751(7)	Ni2–C20	2.087(6)
P2–C251	1.819(8)	Ni2–C21	2.137(6)
P2–C261	1.805(7)	Ni2–C22	2.129(5)
C26–C27	1.453(9)	Ni2–C23	2.187(6)
C27–N28	1.31(1)	Ni2–C24	2.194(6)
N28–N29	1.375(7)		
N29–C25	1.384(9)		
	P2–Ni2–O2	90.3(1)	

[a] See also Table 4.

This study establishes that the phosphinopyrazololato ligand acts as a chelating *P,O* ligand. The molecular structure of complex **3** consists in the juxtaposition of two structurally similar isomers, **3a** and **3b**. One of these isomers, **3a**, is shown in Figure 1. In each isomer the least-squares C_5 of the C_5Ph_5 ring and the P–O–Ni plane are almost perpendicular (dihedral angles: 88.6(2)° in **3a**, 86.7(2)° in **3b**). The oxygen atoms lie transoid to one of the $C_5(Ph_5)$ carbons (see Figure 1). The five-membered *P,O* metallacycles are planar (maximum deviation 0.07 Å in **3a** and 0.08 Å in **3b**) and are coplanar with the corresponding pyrazole ring. The high degree of conjugation, in both isomers, between the *N*-phenyl and the aromatic pyrazolyl rings is exemplified by the relatively small dihedral angle between these planes (11.7° in **3a** and 14.7° in **3b**). The bond lengths and angles of the pyrazole parts are not unusual[11,12] (Table 3). The Ni–P distances (2.205(2) Å in **3a**, 2.213(2) Å in **3b**) are rather long when compared with those of other (phosphinoenolato)nickel complexes (Table 4). This could be related to the strong electron-withdrawing effect of the pyrazolyl group.



3a



3b

The C_5 rings are planar to within 0.03 Å; the high estimated standard deviations within the C_5 ring of **3a** limit somewhat the discussion of the mode of bonding. For the C_5 ring of **3b**, however, it is apparent that there are two short and three long C–C bonds. This situation is reminiscent of that found in $[Ni(\eta^5\text{-}C_5Ph_5)\{Ph_2PCH_2C(O)Ph\}]BF_4$, for which the $(\eta^5\text{-}C_5Ph_5)$ ligand was described as (η^1,η^4)-bonded.[4] The fact that the Ni–C20 bond (transoid to the oxygen atom) of **3b** (and also the Ni–C10 in **3a**) is significantly shorter than the other Ni–$C(C_5)$ bonds emphasizes the possibility of a (η^1,η^4)-bonding mode for the C_5Ph_5 ligand. The more frequently encountered[13–15] allyl–ene bonding mode can however formally not be excluded in isomer **3a**. The phenyl rings of the η^5-coordinated ligand assume the usual[16] propeller type arrangement, each tilted at an angle, relative to the C_5 plane, with $C-C-C_{ipso}-C_{ortho}$ torsion angles ranging from 41.6 ± 0.3 to 52.5 ± 0.3° in **3a** and from 37.5 ± 0.3 to 76.9 ± 0.2° in **3b**.

Table 4. Bond Lengths (Å) in Some *Ni,P,O* Metallacycles

compound	*d*(NiP)	*d*(NiO)	*d*(CO)	*d*(PC)	*d*(CC)
3a	2.205	1.921	1.296	1.764	1.346
3b	2.213	1.921	1.339	1.751	1.38
$[Ni\{Ph_2PCH{=}C(O)Me\}_2]$[11]	2.185	1.893	1.314	1.756	1.357
$[NiPh\{Ph_2PCH{=}C(O)Me\}(PPr_3CH_2)]$[17]	2.176	1.951	1.302	1.761	1.358
$[NiPh\{Ph_2PCH{=}C(O)Ph\}(PPh_3)]$[5]	2.168	1.914	1.313	1.769	1.365
$[Ni\{Ph_2PCH{=}C(O)Ph\}_2]$[18]	2.170	1.86	1.30	1.74	1.38
	2.153	1.88	1.35	1.74	1.37

Complex **3** displays high activity in the low-pressure polymerization of ethene. To be effective, this process requires the presence of sodium borohydride and a temperature of at least 80 °C. In a typical experiment, using an ethene:Ni ratio of 11260 mol:mol ($T = 90$ °C, $P_{90°C} = 38$ bar, Ni:$NaBH_4$ ratio 1:2), 86% of the substrate was converted within 4.5 h, yielding linear olefins (with a selectivity of 97%) of which 87% are α-olefins.[19] With these reaction conditions, the ethene conversion starts after an induction period of ca. 25 min. The activity of this complex is close to that observed for $[Ni(\eta^5\text{-}C_5Ph_5)\{Ph_2PCH{=}C(O)Ph\}]$.[4] By comparison with this latter complex, for which the selectivity in linear α-olefins is ca. 98%, the formation of internal linear olefins is slightly increased. To the best of our knowledge, complex **3** is the first characterized nickel(II) complex suitable for catalytic ethene oligomerization which contains an anionic phosphino–amide chelate.

The catalytic results reported above clearly establish that a three-electron chelating *P,O* ligand bearing a strong electron-withdrawing group has, by comparison with the $[Ph_2PCH{=}C(O)Ph]^-$ ligand, no substantial impact on the activity of nickel complexes toward ethene oligomerization, despite leading to a different selectivity. Furthermore, our experiments demonstrate that additional strong donors in the coordination sphere, such as phosphanes or C-bonded phosphorus ylides, are not necessary to observe a high catalytic activity for (phosphinoenolato)nickel complexes. Further study will concentrate on the mechanism of the catalytic process and especially on the nature of possible hydrido species generated under the conditions defined above as well as the effect of additional ligands or cocatalysts.

Supplementary Material Available: Tables of H atom fractional coordinates, thermal parameters, and bond distances and angles (20 pages). Ordering information is given on any current masthead page.

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