Journal of Organometallic Chemistry, 287 (1985) 419–426
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ORGANONICKEL CHEMISTRY

I. THE CRYSTAL AND MOLECULAR STRUCTURES OF $Ph_3PNi(Ph)(Ph_2PCHCOPh)$ AND *cis*-$Ni(Ph_2PCHCOPh)_2 \cdot 0.5C_7H_8$

HUANG QICHEN, XU MINZHI, QIAN YANLONG*, XU WEIHUA,
Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai (China)

SHAO MEICHENG * and TANG YOUQI
Institute of Physical Chemistry, Peking University, Beijing (China)

(Received August 27th, 1984)

Summary

Reaction of $Ni(Cod)_2$, Ph_3P and $Ph_3PCHCOPh$ in toluene affords $Ph_3PNi(Ph)(Ph_2PCHCOPh)$ (I), but with Ph_3As instead of Ph_3P, it affords *cis*-$Ni(Ph_2PCHCOPh)_2 \cdot 0.5$tol (II). The crystal and molecular structures have been studied by X-ray diffraction. The crystals of I, are monoclinic, space group *Cc*, with a 13.549(7), b 13.775(3), c 19.763(6) Å, β 102.34(3)°, V 3603(2) Å^3, $Z = 4$. The final R factor is 0.070 for 1392 observed reflections. The crystals of II are monoclinic, space group $C2/c$, with a 27.425(7), b 11.113(2), c 24.534(7) Å, β 108.27(2)°, V 7100(3) Å^3, $Z = 8$. The final R factor is 0.083 for 1409 observed reflections.

The coordinations of the nickel atoms in both structures are square planar, and the bond lengths and bond angles in the $\overline{\text{PCCONi}}$ five-membered ring indicate a delocalized system.

Introduction

Nickel complexes with chelate ligands are known to oligomerize ethylene to α-olefins [1,2]. The oligomerization of ethylene to linear α-olefins is of substantial technical interest. The selectivity to obtain the linear α-olefin depends on the structure of the catalyst. In order to study a relation between the structure of the catalyst and the catalytic selectivity to obtain the linear α-olefin in the oligomerization of ethylene, we have prepared a group of nickel complexes with chelate ligands [3,4]. We now wish to report the crystal and molecular structures of the two title complexes. Catalysis studies with a series of nickel complexes including these are in progress.

0022-328X/85/$03.30

Experimental

Preparation

$Ph_3PNi(Ph)(Ph_2PCHCOPh)$ (I) was prepared by the reaction of $Ni(cod)_2$, Ph_3P and $Ph_3PCHCOPh$ in toluene at 0°C, under nitrogen. M.p. 127–129°C. (Found: C, 74.79; H, 5.46. $C_{44}H_{36}OP_2Ni$ calcd.: C, 75.34; H, 5.17%.)

$Ni(Ph_2PCHCOPh)_2$ (II) was prepared by the same method, but Ph_3As was used instead of Ph_3P. M.p. 188–189°C. (Found: C, 72.33; H, 4.89. $C_{40}H_{32}O_2P_2Ni$ calcd.: C, 72.21; H, 4.85%.)

Crystal data and experiment parameters

The crystals of both complexes were obtained by recrystallization from toluene. The crystal was covered with epoxyresin for I, or sealed in a thin wall glass capillary for II, because these two crystals decompose immediately when exposed to air. Diffraction intensities were measured on a Syntex P3/R3 four-circle diffractometer, using Mo-K_α radiation with a graphite monochromator, λ 0.71069 Å. The crystal data and other experimental parameters are listed in Table 1.

The intensities were corrected for Lorentz and polarization effects but not for absorption effects.

TABLE 1

CRYSTAL DATA

Compound	I	II
Formula weight	$C_{44}H_{36}OP_2Ni$/701.4	$C_{43.5}H_{36}O_2P_2Ni$/711.4
Colour and habit	yellow/plates	red/plates
Crystal system	monoclinic	monoclinic
Systematic absences	hkl when $h+k=2n+1$ $h0l$ when $l=2n+1$	hkl when $h+k=2n+1$ $h0l$ when $l=2n+1$
Space group	Cc	$C2/c$
a (Å)	13.549(7)	27.425(7)
b (Å)	13.775(3)	11.113(2)
c (Å)	19.763(6)	24.534(7)
β (°)	102.34(3)	108.27(2)
V (Å^3)	3603(2)	7100(3)
Z	4	8
D_c (g cm^{-3})	1.29	1.33
μ(Mo-K_α) (cm^{-1})	6.6	6.8
F(000)	1464	2968
Scan method	$\theta-2\theta$	$\theta-2\theta$
Max. 2θ (°)	45	40
Crystal size (mm)	0.1×0.1×0.1	0.1×0.1×0.2
Scan rate (° min^{-1})	4–30	7–30
No. of observed reflections	1392 $I > 1.96\sigma(I)$	1409
R	0.070	0.083
R_w	0.054 $w=1/(\sigma^2(F)+0.00025F^2)$	0.066 $w=1/(\sigma^2(F)+0.0003F^2)$
GOF	1.319	1.461

Structure solution and refinement of I

The solution of the structure by direct methods (SOLV or RANT instructions of SHELXTL 3.0 program system) failed. From the Patterson map, the positions of Ni (0, 0.18, 0), P(1) (0.10, 0.18, 0.10) and P(2) (−0.10, 0.18, −0.10) were obtained, but further Fourier synthesis or Karle recycling could not locate any other non-hydrogen atom, due to the pseudo-symmetry between P(1) and P(2) atoms. So, we only used the positions of Ni and P(1), and pre-emphasized the scattering factor of P(1), i.e. we assumed its position to be of the nickel atomic type. Then the structure was solved by ten Karle recycling procedures and refined by full-matrix least-squares method. The hydrogen atoms were introduced into calculated positions (C–H 0.96 Å). Final refinement reduced R to 0.070.

Structure solution and refinement of II

The structure of II was solved readily by the direct method. A difference Fourier synthesis showed the disordered toluene molecule with the ring centre on the $\frac{1}{4},\frac{1}{4},0$ symmetry centre, and the methyl group having four positions with different occupancy parameters, which were adjusted to make the temperature factors almost equal. The hydrogen atoms were located from an accurate difference Fourier map except those of the disordered toluene molecule. The final refinement reduced R to 0.083.

Results and discussion

The molecular structures of compounds I and II are shown in Fig. 1 and 2. Atomic coordinates and temperature factors are listed in Tables 2 and 3 and important bond lengths and angles are listed in Tables 4 and 5, respectively. Hydrogen atomic coordinates and structure factors are available from the authors.

(Continued on p. 424)

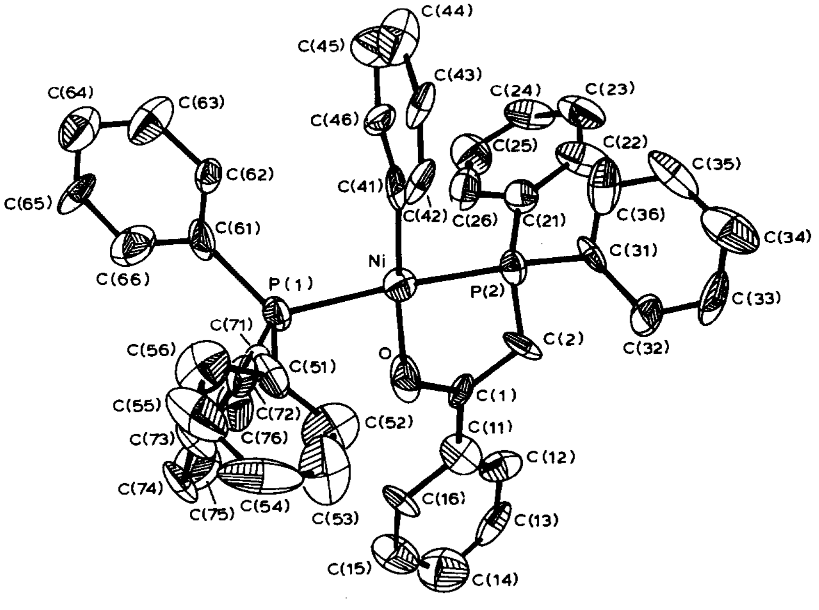

Fig. 1. Molecular structure of $Ph_3PNi(Ph)(Ph_2PCHCOPh)$.

TABLE 2

POSITIONAL $(\times 10^4)$ AND THERMAL $(\times 10^3)$ PARAMETERS FOR I (U_{eq} defined as 1/3 of the trace of the orthogonalized U tensor)

Atom	x	y	z	U_{eq}
Ni	0	1841(2)	0	32(1)
P(1)	1052(4)	2130(3)	1042(3)	36(2)
P(2)	−960(3)	1707(4)	−1016(2)	41(2)
O	−357(7)	3168(8)	−18(6)	58(5)
C(1)	−937(11)	3499(12)	−580(8)	36(6)
C(2)	−1345(14)	2929(11)	−1120(10)	39(8)
C(11)	−1122(14)	4566(12)	−610(9)	54(8)
C(12)	−1488(14)	5081(14)	−1202(11)	56(9)
C(13)	−1620(14)	6054(17)	−1139(11)	72(10)
C(14)	−1325(16)	6607(16)	−561(13)	104(13)
C(15)	−895(16)	6063(16)	19(12)	86(11)
C(16)	−765(14)	5070(13)	29(9)	44(8)
C(21)	−341(11)	1455(12)	−1728(7)	44(7)
C(22)	−777(16)	949(12)	−2300(8)	47(8)
C(23)	−254(17)	834(14)	−2833(10)	72(10)
C(24)	627(17)	1336(14)	−2812(10)	59(10)
C(25)	1100(16)	1879(17)	−2275(9)	79(9)
C(26)	599(11)	1880(15)	−1693(8)	61(8)
C(31)	−2056(13)	950(10)	−1139(7)	42(7)
C(32)	−1931(14)	−41(12)	−1161(7)	51(8)
C(33)	−2786(14)	−634(14)	−1273(8)	66(10)
C(34)	−3756(18)	−328(15)	−1333(10)	81(11)
C(35)	−3825(13)	641(14)	−1306(9)	69(9)
C(36)	−3027(12)	1326(14)	−1217(8)	45(8)
C(41)	362(10)	508(11)	4(8)	35(6)
C(42)	1081(12)	76(13)	−278(8)	44(7)
C(43)	1330(14)	−887(13)	−238(9)	61(9)
C(44)	726(13)	−1521(14)	66(9)	55(8)
C(45)	−38(12)	−1159(14)	321(7)	42(7)
C(46)	−234(12)	−151(13)	289(7)	43(7)
C(51)	299(12)	2019(10)	1717(7)	39(7)
C(52)	−677(14)	2340(13)	1542(10)	66(9)
C(53)	−1154(19)	2216(15)	2057(11)	76(11)
C(54)	−825(15)	1888(12)	2721(10)	88(10)
C(55)	178(15)	1554(14)	2866(8)	78(10)
C(56)	712(16)	1638(13)	2359(8)	63(9)
C(61)	2209(12)	1437(11)	1373(7)	33(6)
C(62)	3128(13)	1878(15)	1653(9)	71(9)
C(63)	3939(16)	1338(17)	1935(11)	73(10)
C(64)	3955(19)	377(19)	1934(11)	91(12)
C(65)	3024(16)	−74(21)	1646(11)	91(12)
C(66)	2190(12)	422(12)	1394(8)	35(7)
C(71)	1459(13)	3391(11)	1126(9)	40(8)
C(72)	1423(12)	3969(11)	1682(9)	47(7)
C(73)	1697(15)	4926(13)	1675(10)	60(8)
C(74)	2025(15)	5274(16)	1115(9)	88(11)
C(75)	2087(14)	4764(14)	552(9)	75(9)
C(76)	1761(12)	3803(13)	579(8)	58(8)

TABLE 3

POSITIONAL ($\times 10^4$) AND THERMAL ($\times 10^3$) PARAMETERS FOR II (U_{eq} defined as 1/3 of the trace of the orthogonalized U tensor)

Atom	x	y	z	U_{eq}
Ni	3816(1)	7501(3)	1367(1)	32(1)
P(1)	3695(2)	9074(5)	816(2)	32(2)
P(2)	4360(2)	6534(5)	1062(2)	37(3)
O(1)	3367(4)	8225(10)	1697(5)	40(6)
O(2)	3825(4)	6179(10)	1846(4)	46(6)
C(1)	3154(6)	9260(14)	1520(6)	19(7)
C(2)	3232(6)	9805(16)	1047(6)	19(7)
C(3)	4111(6)	5217(16)	1803(6)	32(7)
C(4)	4419(6)	5213(16)	1460(6)	23(7)
C(11)	4237(7)	110(16)	929(6)	45(9)
C(12)	4634(7)	120(18)	1433(7)	44(9)
C(13)	5033(8)	920(22)	1606(10)	73(12)
C(14)	4970(6)	1817(16)	1177(9)	67(9)
C(15)	4611(7)	1930(19)	660(9)	68(11)
C(16)	4224(7)	1030(19)	556(8)	48(10)
C(21)	3449(7)	8826(15)	57(7)	40(9)
C(22)	1256(7)	6170(16)	290(7)	52(8)
C(23)	1422(9)	6494(17)	887(9)	62(10)
C(24)	1953(8)	6674(15)	1097(9)	43(10)
C(25)	2271(10)	6648(18)	775(8)	65(11)
C(26)	2081(6)	6399(16)	196(7)	37(7)
C(31)	2811(6)	9784(15)	1810(7)	35(6)
C(32)	2580(7)	921(17)	1676(8)	43(10)
C(33)	2287(6)	1362(20)	1997(7)	47(9)
C(34)	2241(9)	798(22)	2475(10)	56(13)
C(35)	2497(8)	9691(17)	2623(9)	61(12)
C(36)	2777(7)	9179(19)	2280(8)	72(11)
C(41)	4983(5)	7205(15)	1189(6)	33(6)
C(42)	5128(7)	7955(14)	783(9)	47(10)
C(43)	5590(8)	8536(19)	917(10)	72(12)
C(44)	5931(7)	8370(20)	1510(8)	86(12)
C(45)	5799(6)	7661(19)	1889(7)	54(9)
C(46)	5322(6)	7067(15)	1734(7)	33(8)
C(51)	4142(6)	6099(15)	323(7)	32(7)
C(52)	4424(10)	5795(18)	−27(10)	67(13)
C(53)	4234(9)	5348(20)	−558(9)	77(14)
C(54)	3699(7)	5116(18)	−779(8)	68(10)
C(55)	3406(8)	5381(17)	−449(8)	56(10)
C(56)	3574(10)	5938(22)	72(9)	76(13)
C(61)	4011(6)	4108(15)	2105(6)	32(8)
C(62)	4015(6)	2974(14)	1895(7)	48(8)
C(63)	3898(6)	1985(17)	2194(7)	51(10)
C(64)	3713(6)	2199(13)	2664(7)	41(8)
C(65)	3742(7)	3320(18)	2868(9)	61(9)
C(66)	3867(8)	4272(15)	2571(8)	58(9)
C(71)	2884(13)	2377(34)	−196(13)	139(20)
C(72)	3005(16)	2981(28)	257(14)	127(21)
C(73)	2551(24)	2889(37)	313(21)	71(27)
C(74a) [a]	2793(14)	3586(25)	722(15)	173(20)
C(74b) [a]	2158(21)	3342(43)	679(22)	178(31)

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[a] The C(74a) and C(74b) are the positions of the methyl carbon atom in the disordered toluene. Their occupancy factors are 0.3 and 0.2, respectively.

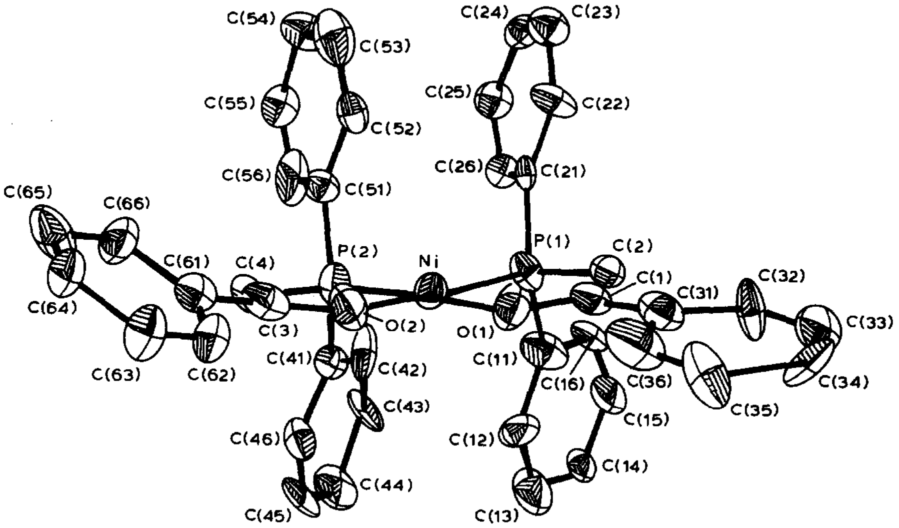

Fig. 2. Molecular structure of $Ni(Ph_2PCHCOPh)_2$.

The molecular structure of complex I is very similar to that in its triclinic crystal form [1]. The nickel atom is surrounded in an almost square planar arrangement by a Ph_3P, a σ-bonded phenyl group and a bidentate ylide ligand bonded to the nickel atom by O and P. The bond angles involving the nickel atom are 93.1(4), 87.4(3), 91.5(4) and 88.0(3)°, which are very close to 90°. The Ni–P(2) bond of 2.155(4) Å is

TABLE 4

SELECTED BOND LENGTHS, ANGLES AND EQUATION OF PLANES IN I

Bond lengths (Å)			
Ni-P(1)	2.275(5)	P(2)-C(2)	1.760(16)
Ni-O	1.890(12)	P(2)-C(21)	1.819(17)
Ni-P(2)	2.155(4)	P(2)-C(31)	1.788(17)
Ni-C(41)	1.899(15)	C(1)-C(2)	1.347(23)
P(1)-C(51)	1.852(18)	C(1)-O	1.299(18)
P(1)-C(61)	1.833(16)	C(11)-C(1)	1.489(23)
P(1)-C(71)	1.818(17)		
Bond angles (°)			
P(1)-Ni-P(2)	174.4(2)	Ni-O-C(1)	117.5(10)
O-Ni-C(41)	179.1(6)	Ni-P(2)-C(2)	97.6(6)
P(1)-Ni-O	87.4(3)	O-C(1)-C(2)	123.0(15)
P(1)-Ni-C(41)	93.1(4)	C(1)-C(2)-P(2)	113.8(12)
P(2)-Ni-O	88.0(3)	C(21)-P(2)-C(31)	106.9(7)
P(2)-Ni-C(41)	91.5(4)		

Equation of plane defined by Ni, P(2), O, C(1) and C(2)

$12.0689\,x + 2.8401\,y - 11.5823\,z = 0.5092$

Deviation (Å) of atom from the plane

Ni	0.0136	P(2)	−0.0077	O	−0.0230
C(1)	0.0196	C(2)	−0.0025		

TABLE 5

SELECTED BOND LENGTHS, ANGLES AND EQUATION OF PLANES IN II

Bond lengths (Å)			
Ni–P(1)	2.170(6)	P(2)–C(41)	1.800(16)
Ni–P(2)	2.153(7)	P(2)–C(51)	1.789(16)
Ni–O(1)	1.857(14)	O(1)–C(1)	1.301(19)
Ni–O(2)	1.877(11)	O(2)–C(3)	1.349(21)
P(1)–C(2)	1.743(18)	C(1)–C(2)	1.385(24)
P(1)–C(11)	1.832(19)	C(1)–C(31)	1.467(26)
P(1)–C(21)	1.793(17)	C(3)–C(4)	1.368(26)
P(2)–C(4)	1.742(18)	C(3)–C(61)	1.506(14)
Bond angles (°)			
P(1)–Ni–P(2)	100.0(2)	Ni–O(1)–C(1)	121.8(12)
P(1)–Ni–O(1)	85.9(4)	Ni–O(2)–C(3)	117.8(11)
P(1)–Ni–O(2)	171.8(4)	O(1)–C(1)–C(2)	119.7(16)
P(2)–Ni–O(1)	173.9(4)	O(2)–C(3)–C(4)	122.4(16)
P(2)–Ni–O(2)	87.2(4)	P(1)–C(2)–C(1)	112.8(12)
O(1)–Ni–O(2)	86.9(5)	P(2)–C(4)–C(3)	112.1(13)
Ni–P(1)–C(2)	99.1(6)	C(11)–P(1)–C(21)	106.0(8)
Ni–P(2)–C(4)	100.3(7)	C(41)–P(2)–C(51)	106.5(8)

Equation of defined by Ni, P(1), P(2), O(1) and O(2)

$15.6997x + 4.9058y + 11.6941z = 11.2540$

Deviation (Å)of atom from the plane

Ni	0.0167	P(1)	−0.0473	P(2)	0.0383
O(1)	0.0514	O(2)	−0.0591		

shorter than the normal Ni–P single-bond 2.26 Å [5], and has double-bond character. The bonds P(2)–C(2), C(2)–C(1) and C(1)–O are 1.76(2), 1.35(2) and 1.30(2) Å. However, in the free ylide $Ph_3PCHCOPh$ [6], these values are 1.71, 1.39 and 1.26 Å, respectively. These facts indicate a delocalized Ni–P(2)–C(2)–C(1)–O system, which conjugates with C(11) to C(16) of the phenyl ring through the C(1)–C(11) bond (1.49 Å). The Ni–C(41) bond is unusually short (1.90 Å), the observed values in some other cases are 1.96–2.0 Å [7]. The bond angle C(2)–P(2)–Ni is 97.6°, which is far from 109.5°, as required by sp^3 hybridization. It is assumed that besides the P(2)–C(2) bond along the bond-axis (x-axis), the appropriate $3d_{xz}$ orbital of P(2) can overlap with the $2p_z$ orbital of C(2) to form a d–p π-bond. Simultaneously, its $3d_{yz}$ orbital can overlap with the $3d_{yz}$ orbital of Ni to form another d–d π-bond.

In complex II, the nickel atom is surrounded in a square-planar arrangement by two bidentate ylide ligands. But owing to the repulsion between phenyl groups attached to the two *cis*-phosphorus atoms, the bond angle P(1)–Ni–P(2) is 100.0°. The angle between the plane defined by Ni,P(1),O(1) and the plane defined by Ni,P(2),O(2), is only 4.5°. So, these two oxygen atoms and two phosphorus atoms are almost coplanar, and form a trapezoid, but not a flattened tetrahedron. Because complex II has two delocalized five-membered-rings, it should be more stable than complex I, which has been observed.

Acknowledgements

Financial assistance from the Science Fund of the Chinese Academy of Sciences, is gratefully acknowledged.

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