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Crystal and Molecular Structure of (Ethyl methacrylate)-bis(triphenylphosphine)nickel(0)

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The crystal and molecular structure of (ethyl methacrylate)bis(triphenylphosphine)nickel, (CH_2=C(CH_3)-$COOC_2H_5$) $(PPh_3)_2Ni$, has been determined by single-crystal X-ray analysis. The crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions a=13.690(2), b=16.855(2), c=15.699(1)Å, β=105.09(1)°, and Z=4. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares technique, using 4701 independent reflections, the final R value being 0.084 for $|F_o| \geq 3\sigma(F)$. The two phosphine ligands and the two olefinic carbon atoms comprise a distorted square-planar configuration about the Ni atom. The Ni–β-CH_2 bond (1.976(8)Å) is significantly shorter than the Ni–α-C bond (2.029(7)Å). The difference is explained by the contribution of polarized resonance structure in metal-olefin bonding.

Interaction of olefins with transition metals is of particular importance in organometallic and catalytic chemistry. Although extensive structural studies by X-ray analysis have been done on the group VIII transition metal complexes coordinated with olefins,[1-4] reports concerning nickel olefin complexes are rather limited, because of their thermal instability and high reactivity toward oxygen.[2-4] On the other hand, no report on the crystal structure of transition metal–α,β-unsaturated ester π complexes has been made to our knowledge[5] except for a Ru(0) complex with ethyl methacrylate, in which C–H oxidative addition of the ligand to Ru(0) has been found to give an unusual hydrido vinyl complex.[6]

We have studied the reactivities of zero valent nickel complexes with various vinyl compounds and found that the reaction of bis(1,5-cyclooctadiene)nickel with α,β-unsaturated ester (ethyl methacrylate, methyl methacrylate *etc.*) in the presence of tertiary phosphine ligands gives a convenient preparative method of various zerovalent nickel olefin complexes,[7] and the coordination through C=C bond has been postulated from the NMR and IR analyses and their chemical reactions.[8]

In order to get information concerning the bonding mode between nickel and α,β-unsaturated ester, an X-ray analysis of the (ethyl methacrylate)bis(triphenylphosphine)-nickel(0) crystal has been performed.

Experimental

(Ethyl methacrylate)bis(triphenylphosphine)nickel(0) was synthesized by the method previously reported.[7] A crystal suitable for X-ray diffraction, obtained by slow recrystallization from toluene at room temperature under nitrogen, was sealed in a capillary. Density of the crystal was determined by floatation in a mixture of CCl_4 and decalin. Data collection was carried out with a Rigaku computer-controlled four-circle diffractometer, using graphite-monochromated Cu $K\alpha$ radiation (λ=1.54178 Å) The unit-cell parameters were calculated with 37 high angle reflections. The crystallographic data are summarized in Table 1. Intensities were measured in ω-2θ scan mode with scan width of 1.5° (in ω) plus α_1-α_2 divergence at scan speed 4° (in 2θ) min^{-1}. Four reference reflections indicated no significant intensity variations throughout the experiment. Out of 4701 independent reflections in the range $5<2\theta<115°$, 362 weak reflections which gave the counts under background were considered as zero-reflections. The data were corrected for Lorentz and polarization factors but not for absorption effects. The standard deviation for each reflection was estimated by the equation, $\sigma^2(F)=\sigma_p^2+q|F_o|^2$, where σ_p is due to counting statistics and q is 4.39×10^{-6}, derived from the variation of the monitored reflections.

TABLE 1. CRYSTAL DATA

Compound	$Ni(CH_2=C(CH_3)COOC_2H_5)(PPh_3)_2$
Formula weight	697.53
Formula	$C_{42}H_{40}O_2P_2Ni$
Crystal system	Monoclinic
Space group	$P2_1/c$
a	13.690(2) Å
b	16.855(2) Å
c	15.699(1) Å
β	105.09(1)°
V	3497.7(6) Å^3
Z	4
Density	
exptl	1.31 g·cm^{-3}
calcd	1.32 g·cm^{-3}

Structure Determination

The structure was solved by the heavy-atom method and the atomic parameters were refined by block-diagonal least-squares technique. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$, with $w=1/\sigma^2(F)$. All the hydrogen atoms assigned on a difference map were included. The zero reflections were included in the least-squares calculation by assuming $|F_o|=F_{lim}$ where F_{lim} is 2.67, an observational threshold value, but those for which $|F_c|<F_{lim}$ were omitted. The final R was 0.098 (R=0.084 for $|F_o|>3\sigma(F)$). The final atomic parameters are listed in Table 2.[9] Atomic scattering factors used were taken from International Tables for X-ray Crystallography.[10]

Table 2. Fractional coordinates ($\times 10^5$; for H, $\times 10^3$) and thermal parameters ($\times 10^4$(/Å^2); for H, $\times 10^3$(/Å^2))

The anisotropic temperature factor has the form: $\exp\{-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\}$. The isotropic temperature factor has the form: $\exp\{-(8\pi^2U)\sin^2\theta/\lambda^2\}$.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
NI	79607(8)	50371(6)	31970(7)	506(6)	331(5)	759(7)	27(5)	131(5)	28(6)
P(1)	81023(13)	54132(9)	19105(12)	236(10)	171(8)	484(12)	2(8)	95(9)	13(8)
P(2)	72321(13)	59509(10)	38074(12)	275(10)	196(9)	441(12)	18(8)	87(9)	-3(8)
C(1)	86716(54)	40072(40)	33059(53)	406(47)	298(41)	852(62)	215(36)	164(43)	168(40)
C(2)	82667(51)	41033(36)	40401(45)	413(45)	221(37)	516(49)	94(33)	43(36)	119(33)
C(3)	89907(64)	42334(47)	49602(54)	683(63)	550(57)	677(63)	109(46)	-141(48)	185(45)
C(4)	73223(55)	37672(37)	40840(49)	530(51)	189(37)	712(58)	53(34)	180(43)	97(35)
C(5)	56719(71)	33907(59)	32337(73)	576(67)	869(77)	1461(101)	-345(58)	4(64)	98(68)
C(6)	50064(81)	35449(67)	23945(80)	790(84)	1082(90)	1664(119)	-287(72)	-156(77)	30(85)
C(7)	70888(50)	60364(37)	12223(44)	352(42)	286(38)	455(47)	25(32)	105(35)	62(33)
C(8)	69872(52)	68207(40)	14657(46)	347(44)	396(44)	517(52)	77(35)	14(38)	72(35)
C(9)	61556(59)	72673(42)	10147(56)	482(53)	374(46)	893(66)	87(39)	247(48)	160(43)
C(10)	54118(56)	69456(45)	3712(56)	325(47)	521(52)	890(68)	19(39)	25(44)	309(46)
C(11)	55019(57)	61776(50)	1292(53)	396(50)	752(62)	667(61)	-189(45)	-78(43)	165(47)
C(12)	63331(53)	57232(41)	5481(47)	399(47)	401(45)	549(53)	-54(36)	-7(39)	47(37)
C(13)	81564(46)	46349(35)	11080(41)	261(38)	288(36)	336(42)	46(30)	90(31)	36(31)
C(14)	86670(54)	46973(38)	5007(48)	445(48)	303(40)	609(54)	-65(34)	134(40)	-96(35)
C(15)	86604(59)	41066(47)	-1296(52)	548(56)	679(57)	642(59)	87(45)	290(46)	-74(45)
C(16)	80852(59)	34248(43)	-1063(50)	559(54)	454(48)	622(58)	6(40)	127(44)	-245(41)
C(17)	75740(58)	33435(42)	4860(51)	535(55)	370(45)	712(61)	-98(39)	76(45)	-128(40)
C(18)	75769(53)	39388(42)	11209(50)	381(47)	459(47)	710(59)	-30(38)	179(41)	-53(41)
C(19)	92442(47)	59844(35)	19544(44)	273(38)	220(34)	511(47)	22(30)	154(33)	-13(32)
C(20)	101236(52)	57783(38)	25921(48)	381(46)	347(43)	637(55)	44(35)	143(40)	105(37)
C(21)	109972(52)	62183(43)	27223(51)	270(43)	496(50)	766(61)	34(36)	82(40)	86(42)
C(22)	110158(54)	68768(41)	21934(52)	341(44)	378(44)	764(61)	-71(35)	179(41)	-77(40)
C(23)	101805(54)	70838(38)	15547(50)	429(48)	264(40)	710(58)	5(34)	229(42)	34(36)
C(24)	93019(48)	66311(38)	14310(44)	295(42)	324(40)	483(48)	5(32)	72(35)	-11(34)
C(25)	58706(49)	60913(35)	33176(45)	310(41)	214(37)	559(50)	-12(31)	118(35)	34(33)
C(26)	52363(55)	64733(43)	37282(52)	366(47)	415(47)	814(63)	-9(37)	143(43)	-164(42)
C(27)	42028(63)	65581(47)	32885(65)	534(59)	496(55)	1387(89)	106(44)	471(60)	-72(55)
C(28)	38220(59)	62575(48)	24839(57)	408(53)	613(58)	957(73)	-27(43)	52(48)	165(50)
C(29)	44325(59)	58726(50)	20695(52)	496(55)	815(64)	622(60)	-199(47)	131(45)	110(48)
C(30)	54560(53)	57717(42)	24833(48)	356(45)	501(48)	571(54)	-66(37)	130(39)	28(39)
C(31)	72879(52)	58524(35)	49649(45)	485(48)	194(36)	494(48)	17(32)	173(38)	-19(32)
C(32)	80519(57)	62012(41)	56296(49)	542(54)	409(46)	596(56)	24(39)	165(43)	46(39)
C(33)	81115(67)	60850(47)	65013(51)	866(70)	564(55)	505(57)	49(49)	8(48)	-40(43)
C(34)	74235(75)	56407(49)	67472(53)	1283(89)	574(57)	500(58)	132(56)	378(59)	158(44)
C(35)	66586(74)	52851(47)	61245(57)	1072(79)	514(55)	685(64)	-181(51)	351(57)	103(45)
C(36)	66115(62)	53881(43)	52650(49)	737(61)	404(45)	536(54)	-28(42)	230(46)	-14(39)
C(37)	78083(47)	69473(34)	38223(44)	265(39)	179(35)	539(50)	-45(29)	93(35)	-51(31)
C(38)	87492(52)	69989(39)	37307(48)	368(45)	351(43)	569(54)	-29(35)	75(39)	-129(36)
C(39)	92670(56)	77187(44)	37764(52)	391(50)	539(51)	698(61)	-127(40)	197(44)	-93(43)
C(40)	87385(63)	83865(43)	38995(53)	711(62)	391(47)	696(61)	-251(43)	111(49)	-30(41)
C(41)	78188(58)	83651(40)	39937(53)	520(53)	282(42)	855(65)	-12(37)	181(47)	11(40)
C(42)	72963(54)	76483(39)	39450(50)	386(48)	337(41)	730(58)	55(35)	258(42)	15(39)
O(1)	70595(44)	35937(30)	47301(37)	923(47)	498(35)	880(46)	-39(33)	433(37)	192(31)
O(2)	66807(40)	36725(31)	32507(36)	596(39)	597(37)	877(45)	-299(31)	2(33)	93(32)

ATOM	X	Y	Z	U	ATOM	X	Y	Z	U
H(31)	962(5)	438(4)	481(5)	53(25)	H(201)	1000(5)	548(4)	300(4)	33(21)
H(32)	924(5)	388(4)	528(5)	55(26)	H(211)	1158(5)	612(4)	321(4)	50(25)
H(33)	859(5)	461(4)	539(4)	41(23)	H(221)	1154(5)	718(4)	209(4)	43(23)
H(61)	412(7)	335(6)	231(6)	112(38)	H(231)	1019(5)	753(3)	113(4)	8(17)
H(62)	553(7)	335(6)	211(6)	111(38)	H(241)	870(4)	672(3)	103(3)	0(16)
H(63)	517(8)	400(6)	212(7)	141(44)	H(261)	550(4)	663(3)	427(3)	3(16)
H(51)	581(8)	289(6)	372(7)	131(43)	H(271)	392(5)	667(4)	364(4)	30(21)
H(52)	537(7)	377(6)	379(6)	111(37)	H(281)	306(6)	618(5)	220(6)	98(35)
H(11)	936(4)	404(3)	331(3)	2(16)	H(291)	422(5)	575(4)	152(4)	22(19)
H(12)	829(5)	361(4)	268(4)	51(25)	H(301)	586(4)	551(3)	212(3)	0(15)
H(81)	749(4)	702(3)	188(3)	0(16)	H(321)	842(4)	644(3)	545(3)	2(16)
H(91)	599(5)	773(4)	123(4)	41(23)	H(331)	835(4)	628(3)	674(3)	0(16)
H(101)	476(5)	726(4)	15(4)	29(21)	H(341)	742(5)	557(3)	724(4)	16(18)
H(111)	508(4)	597(3)	-23(4)	17(19)	H(351)	621(4)	505(4)	625(4)	20(18)
H(121)	650(5)	535(4)	28(4)	31(21)	H(361)	614(5)	518(4)	473(4)	43(24)
H(141)	903(4)	502(3)	42(3)	3(15)	H(381)	903(5)	665(4)	351(4)	39(23)
H(151)	905(4)	412(3)	-53(3)	0(16)	H(391)	993(4)	775(3)	364(4)	8(17)
H(161)	816(4)	316(3)	-51(4)	5(16)	H(401)	893(4)	868(3)	388(3)	1(16)
H(171)	719(5)	300(3)	52(4)	17(19)	H(411)	746(5)	863(4)	411(4)	28(20)
H(181)	722(4)	389(3)	145(3)	0(16)	H(421)	676(4)	764(3)	408(3)	0(16)

Results and Discussion

As shown in Fig. 1, the crystal structure consists of discrete molecules. All intermolecular contacts are normal, the shortest being 2.35 Å between H031 atoms related by the inversion center at (1,½, ½). Figure 2 shows a stereo view of the molecule. Tables 3 and 4 list the bond lengths and bond angles, respectively. All the C–C bond lengths and the C–C–C angles of the phenyl rings are normal, although some of these are contracted seemingly by the large thermal motion. The P–C bond distances and the Ni–P–C and C–P–C angles are comparable with those of the related compounds.[2-4]

As shown in Fig. 3, the nickel atom has a distorted square planar coordination of the two C and two P atoms, similar to the related Ni–ethylene complexes, $Ni(C_2H_4)L_2$.[2-4] Although the ethyl methacrylate molecule could coordinate in a variety of modes (*i.e.* through C=C, C=O, or both), only the carbon–carbon double bond has a linkage with the nickel atom, and the

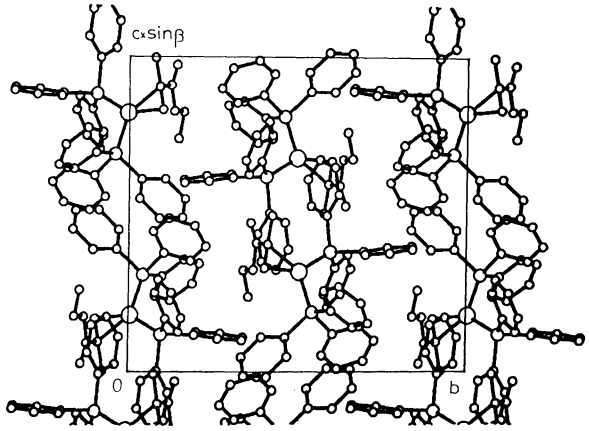

Fig. 1. Molecular packing projected along the a axis.

carbonyl group of the ester turns away from nickel. It seems to be reasonable that the C=C bond lies in the square coordination plane of zero valent metal olefin complex, M(olefin)L_2.[1b]

The coordination mode of ethyl methacrylate ligand mentioned above explains the NMR and IR results reasonably.[7] The large upfield shifts of olefinic protons and carbons in ^{1}H- and ^{13}C-NMR spectra are due to the strong interaction of nickel with the olefinic double bond. The absence of direct interaction between Ni and C=O group supports the slight shifts of ν(C=O) upon coordination.[7,8] The two methylene protons of the ethoxy group, H(51) and H(52), lie in the different circumstances, as indicated by ^{1}H-NMR spectra.[8]

The mean plane of the coordination is expressed by the equation, $0.8841X+0.4174Y+0.2101Z=13.322$ where X, Y, and Z are in Å taken along the directions a^*, b, and c, respectively. The deviations of atoms from the plane are −0.02 (Ni), −0.02 (P(1)), 0.03 (P(2)), 0.07 (C(1)), and −0.06 Å (C(2)). These slight but significant deviations are also described by the dihedral angle of 6.4(4)° between the planes through Ni, P(1), and P(2), and through Ni, C(1), and C(2). In the related Ni(0) and Pt(0) olefin complexes, the dihedral angles range from 1.3 to 18.5°.[2b] Such a twist may be mainly due to a steric effect between the bulky ligand molecules in addition to an electronic effect. The two Ni–P bond distances (2.173 Å and 2.187 Å), the P(1)–Ni–P(2) angle (111.29), the average of the Ni–C bond distances

Table 3. Bond distances (1/Å) and their standard deviation for the heavy atoms

Ni-P(1)	2.173(2)	Ni-P(2)	2.187(2)
Ni-C(1)	1.976(8)	Ni-C(2)	2.029(7)
C(1)-C(2)	1.412(10)	C(2)-C(3)	1.540(11)
C(2)-C(4)	1.430(10)	C(4)-O(1)	1.197(9)
C(4)-O(2)	1.382(9)	C(5)-O(12)	1.454(12)
C(5)-C(6)	1.417(16)		
Triphenylphosphine Ligands			
P(1)-C(7)	1.848(7)	C(7)-C(8)	1.393(10)
C(8)-C(9)	1.394(11)	C(9)-C(10)	1.347(11)
C(10)-C(11)	1.364(11)	C(11)-C(12)	1.387(11)
C(12)-C(7)	1.378(10)		
P(1)-C(13)	1.834(6)	C(13)-C(14)	1.325(10)
C(14)-C(15)	1.402(11)	C(15)-C(16)	1.399(11)
C(16)-C(17)	1.308(11)	C(17)-C(18)	1.408(11)
C(18)-C(13)	1.420(10)		
P(1)-C(19)	1.822(7)	C(19)-C(20)	1.395(9)
C(20)-C(21)	1.377(10)	C(21)-C(22)	1.390(11)
C(22)-C(23)	1.354(10)	C(23)-C(24)	1.392(10)
C(24)-C(19)	1.380(9)		
P(2)-C(25)	1.837(7)	C(25)-C(26)	1.369(10)
C(26)-C(27)	1.411(12)	C(27)-C(28)	1.335(12)
C(28)-C(29)	1.351(12)	C(29)-C(30)	1.393(10)
C(30)-C(25)	1.393(10)		
P(2)-C(31)	1.806(7)	C(31)-C(32)	1.400(10)
C(32)-C(33)	1.364(11)	C(33)-C(34)	1.336(12)
C(34)-C(35)	1.371(13)	C(35)-C(36)	1.345(12)
C(36)-C(31)	1.385(10)		
P(2)-C(37)	1.853(7)	C(37)-C(38)	1.336(10)
C(38)-C(39)	1.398(11)	C(39)-C(40)	1.379(11)
C(40)-C(41)	1.306(11)	C(41)-C(42)	1.396(11)
C(42)-C(37)	1.412(10)		

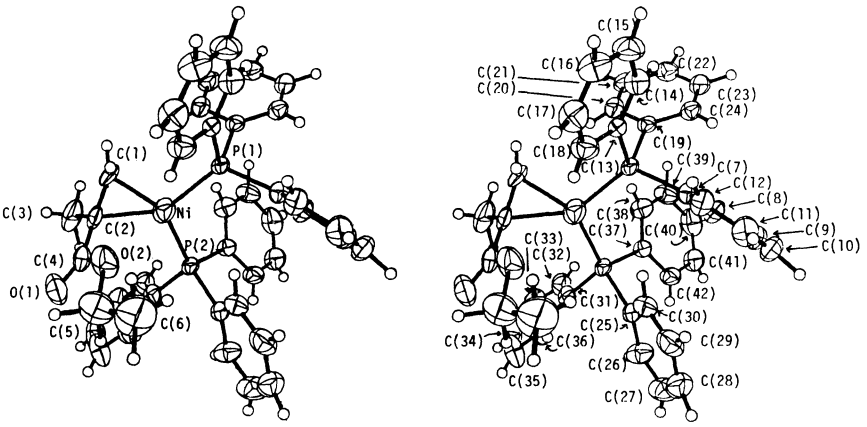

Fig. 2. Stereoscopic drawing of the molecule of (ethyl methacrylate)bis(triphenylphosphine)nickel. The non-hydrogen atoms are represented by their thermal ellipsoids with 50% probability, while the hydrogen atoms are represented by spheres of a fixed arbitrary radius.

Table 4. Bond angles (θ/°) and their standard derivations for the heavy atoms

P(1)-Ni-P(2)	111.3(1)	P(1)-Ni-C(1)	100.1(2)	P(1)-Ni-C(2)	141.1(2)
P(2)-Ni-C(1)	148.4(2)	P(2)-Ni-C(2)	107.5(2)	C(1)-Ni-C(2)	41.3(3)
Ni-P(1)-C(7)	118.3(2)	Ni-P(1)-C(13)	117.3(2)	Ni-P(1)-C(19)	113.7(2)
C(7)-P(1)-C(13)	99.4(3)	C(7)-P(1)-C(19)	103.2(3)	C(13)-P(1)-C(19)	102.5(3)
Ni-P(2)-C(25)	115.9(2)	Ni-P(2)-C(31)	118.1(2)	Ni-P(2)-C(37)	113.7(2)
C(25)-P(2)-C(31)	101.9(3)	C(25)-P(2)-C(37)	105.7(3)	C(31)-P(2)-C(37)	99.5(3)
Ni-C(1)-C(2)	71.4(4)	Ni-C(2)-C(1)	67.4(4)	Ni-C(2)-C(3)	118.3(5)
Ni-C(2)-C(4)	107.7(5)	C(1)-C(2)-C(3)	119.2(6)	C(1)-C(2)-C(4)	123.1(6)
C(3)-C(2)-C(4)	112.4(6)	C(2)-C(4)-O(1)	127.8(7)	C(2)-C(4)-O(2)	111.1(6)
O(1)-C(4)-O(2)	121.1(7)	C(6)-C(5)-O(2)	109.6(9)	C(4)-O(2)-C(5)	114.9(6)
Phenyl Rings					
P(1)-C(8)-C(8)	119.5(5)	P(1)-C(7)-C(12)	122.0(5)	C(8)-C(7)-C(12)	117.8(6)
C(7)-C(8)-C(9)	120.0(7)	C(8)-C(9)-C(10)	121.4(7)	C(9)-C(10)-C(11)	119.0(8)
C(10)-C(11)-C(12)	121.0(7)	C(7)-C(12)-C(11)	120.8(7)		
P(1)-C(13)-C(14)	124.1(5)	P(1)-C(13)-C(18)	117.3(5)	C(14)-C(13)-C(18)	118.5(6)
C(13)-C(14)-C(15)	122.9(7)	C(14)-C(15)-C(16)	117.7(7)	C(15)-C(16)-C(17)	120.6(7)
C(16)-C(17)-C(18)	122.1(7)	C(13)-C(18)-C(17)	118.2(7)		
P(1)-C(19)-C(20)	117.9(5)	P(1)-C(19)-C(24)	125.2(5)	C(20)-C(19)-C(24)	116.9(6)
C(19)-C(20)-C(21)	121.8(7)	C(20)-C(21)-C(22)	119.5(7)	C(21)-C(22)-C(23)	120.1(7)
C(22)-C(23)-C(24)	119.8(7)	C(19)-C(24)-C(23)	121.9(6)		
P(2)-C(25)-C(26)	124.2(5)	P(2)-C(25)-C(30)	117.7(5)	C(26)-C(25)-C(30)	118.1(6)
C(25)-C(26)-C(27)	119.7(7)	C(26)-C(27)-C(28)	121.3(8)	C(27)-C(28)-C(29)	120.0(8)
C(28)-C(29)-C(30)	120.5(8)	C(25)-C(30)-C(29)	120.4(7)		
P(2)-C(31)-C(32)	122.6(5)	P(2)-C(31)-C(36)	122.5(6)	C(32)-C(31)-C(36)	114.8(7)
C(31)-C(32)-C(33)	121.7(7)	C(32)-C(33)-C(34)	120.5(8)	C(33)-C(34)-C(35)	120.3(8)
C(34)-C(35)-C(36)	119.2(8)	C(31)-C(36)-C(35)	123.5(8)		
P(2)-C(37)-C(38)	118.5(5)	P(2)-C(37)-C(42)	122.4(5)	C(38)-C(37)-C(42)	119.1(6)
C(37)-C(38)-C(39)	122.8(7)	C(38)-C(39)-C(40)	116.0(7)	C(39)-C(40)-C(41)	123.4(8)
C(40)-C(41)-C(42)	120.9(7)	C(37)-C(42)-C(41)	117.8(7)		

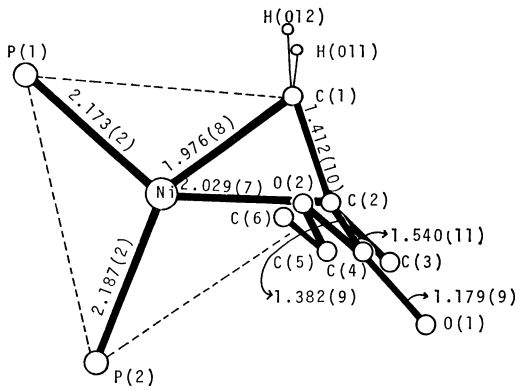

Fig. 3. Coordination geometry around the nickel for (ethyl methacrylate)bis(triphenylphosphine)nickel.

(2.003 Å), and the C(1)–Ni–C(2) angle (41.3°) are comparable with those of the Ni–ethylene complex.[2a-b]

A closer examination, however, shows that the two Ni–C bonds are significantly different, the Ni–C(1) bond distance (1.976 Å) being shorter than Ni–C(2) bond distance (2.029 Å) (Figure 3). The C(1)=C(2) bond is lengthened, whereas the C(2)–C(4) bond is shortened from the normal distances (1.36 Å for C=C and 1.44 Å for C–C in C=C–C=O system)[12]. Although the C(4)–O(1) distance is contracted apparently due to the large thermal motion, a value corrected by the riding model[13] is 1.231 Å. These distances are

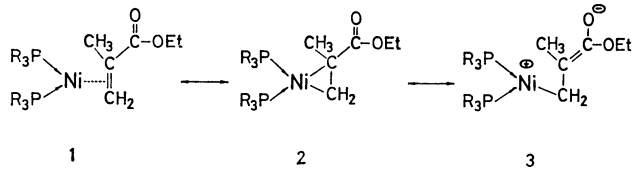

Fig. 4. Some possible resonance structures for (ethyl methacrylate)bis(triphenylphosphine)nickel.

interpreted by the contribution from three-membered metallacycle **2** and polarized structure **3**, in addition to **1** (see Figure 4)†. This scheme is consistent with the observation in ^{13}C-NMR spectra, that the chemical shift of C(1) varies to a higher field more significantly than that of C(2) with increasing the σ-donor property of tertiary phosphine ligands.[8] In addition the steric effect of the two substituents (methyl and ethoxycarbonyl) attached to C(2) and the two bulky triphenylphosphine ligands may facilitate the unequal coordination mentioned above. These two substituents are bent back away from nickel: the deviation of C(2) from the plane of C(1), C(3), and C(4) is 0.195 Å.

† Similar ionic contribution has been reported by Ibers *et al.* for a platinum(0) 1,1-dichloro-2,2-dicyanoethylene complex.[11] On the contrary, olefin shift to maximize the metal–olefin bond is postulated for Ni–acrylonitrile bond.[3] In the present complex a similar sliding of the olefin along the C=C bond is observed

This geometry suggests an increase of sp^3 character of C(1) and C(2).††

The Ni–P(2) distance is slightly longer than that of Ni–P(1) probably owing to the trans influence of closer C(1) to Ni than C(2).

Figure 1 was drawn by TSD:XTAL which is an interactive modeling program system for computer graphics.[14]

References

1) a) M. Herberhold, "Metal π-Complexes, Vol. II, Part 2," Elsevier Sci. Co., London, New York (1974); b) F. G. A. Stone and R. West, "Advances in Organometallic Chemistry," Academic Press, New York, London (1976), Vol. 14, p. 33.

2) a) P. T. Cheng, C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *Acta Crystallogr., Sect B*, **27**, 1904 (1974); b) W. Dreissig and H. Dietrich, *Acta Crystallogr., Sect. B*, **24**, 108 (1968); c) C. Krüger and Y. H. Tsay, *J. Organomet. Chem.*, **34**, 587 (1972).

3) L. J. Guggenberger, *Inorg. Chem.*, **12**, 499 (1973).

4) S. D. Ittel and J. A. Ibers, *J. Organomet. Chem.*, **74**, 121 (1974).

5) Private Communication, recently Krüger solved the crystal structure of a nickel acrylic ester complex with 2,2′-bipyridine and showed the coordination through C=C double bond to nickel.

6) S. Komiya, T. Ito, M. Cowie, A. Yamamoto, and J. A. Ibers, *J. Am. Chem. Soc.*, **98**, 3874 (1976).

7) J. Ishizu, T. Yamamoto, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2646 (1978).

8) T. Yamamoto, J. Ishizu, S. Komiya, Y. Nakamura, and A. Yamamoto, *J. Organomet. Chem.*, **171**, 103 (1979).

9) A list of the observed and calculated structure factors are kept in the Office of the Chemical Society of Japan, (Document No. 8020).

10) "International Tables for X-Ray Crystallography," Vol. IV, The Kynoch Press, Birmingham (1974).

11) A. McAdam, J. N. Francis, and J. A. Ibers, *J. Organomet. Chem.*, **29**, 149 (1971).

12) "Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement," ed by L. E. Sutton, The Chemical Society, London (1965).

13) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

14) A. Takenaka and Y. Sasada, *J. Cryst. Soc. Jpn.*, **21**, 214 (1980).

15) T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, **101**, 3801 (1979).

†† Recently molecular orbital consideration for the problem of asymmetry in metal–olefin bonding has been reported.[15]