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Crystal Structures of (Acrylonitrile)bis(tri-*o*-tolyl phosphite)nickel and (Ethylene)bis(tri-*o*-tolyl phosphite)nickel

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The crystal and molecular structures of (acrylonitrile)bis(tri-*o*-tolyl phosphite)nickel, $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$, and (ethylene)bis(tri-*o*-tolyl phosphite)nickel, $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$, have been determined by single-crystal X-ray techniques. Both structures have a nickel atom trigonally coordinated to two phosphite ligands and an olefin that is nearly in the PNiP plane; the dihedral angles between the Ni-olefin and Ni-P planes are 3.9 (1)° for the acrylonitrile complex and 6.6 (11)° for the ethylene complex. The Ni-P distances in the acrylonitrile complex are 2.121 (4) and 2.096 (4) Å; the Ni-C distances are 2.016 (10) and 1.911 (12) Å. The average Ni-P and Ni-C distances in the ethylene complex are 2.095 (2) and 2.02 (2) Å. The olefin C-C bond length is 1.46 (2) Å for both complexes. The acrylonitrile, in addition to being more strongly bound to nickel than ethylene, is shifted relative to the ethylene geometry to maximize the CN involvement in the Ni-olefin bonding. Comparisons are made between the acrylonitrile and ethylene-phosphite structures and that of (ethylene)bis(triphenylphosphine)nickel for structural correlations with the steric and electronic differences in the molecules. Crystals of $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ are monoclinic, space group $P2_1/c$, with cell dimensions of $a = 17.143$ (9), $b = 12.087$ (9), $c = 19.806$ (20) Å, and $\beta = 91.09$ (14)°. The R factor is 0.097 for the least-squares refinement of 2182 observed reflections. Crystals of $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ are monoclinic, space group Pc, with cell dimensions of $a = 11.812$ (4), $b = 9.823$ (4), $c = 18.337$ (9) Å, and $\beta = 109.50$ (9)°. The R factor for 2059 observed reflections is 0.088.

Introduction

A fairly large number of metal-olefin structures have been determined by diffraction techniques, but there are few systematic structural studies bearing on the nature of the metal-olefin bonding. It is frequently difficult to sort out the parameters influencing metal-olefin bonding in observed X-ray structures because of large inherent differences in the molecules. Details in metal-olefin geometries are influenced by the nature of the metal atom, the olefin ligand, and the remaining ligand atoms, usually phosphines, attached to the metal atom. The crystal structures of (acrylonitrile)bis(tri-*o*-tolyl phosphite)nickel, $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$, and (ethylene)bis(tri-*o*-tolyl phosphite)nickel, $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$, along with the data for (ethylene)bis(triphenylphosphine)nickel, $(C_2H_4)Ni[(C_6H_5)_3P]_2$,[1,2] enable us to make some systematic comparisons in the Ni(0) system of the effects of changing phosphorus ligands and olefin substituents. The Ni(0) system was chosen for this investigation because of other studies being done on this system in our laboratory.[3-5]

Experimental Section

Cell and Intensity Data for $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$. Crystals are monoclinic with cell dimensions of $a = 17.143$ (9), $b = 12.087$ (9), $c = 19.806$ (20) Å, and $\beta = 91.09$ (14)°. These cell parameters resulted from the least-squares refinement of 12 reflections carefully centered on a diffractometer with a low takeoff angle and without the monochromator used for data collection. The systematic extinctions of $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, are characteristic of the space group $P2_1/c$. The calculated density for four molecules per cell is 1.30 g/cm^3. The density could not be measured because the crystals had to be handled in a drybox and they either dissolved or reacted with most solvents. This calculated density, however, is very close to that calculated for $(C_2H_4)Ni[o\text{-}CH_3C_6H_4O)_3P]_2$ (1.31 g/cm^3) and $(C_2H_4)Ni[(C_6H_5)_3P]_2$ (1.28 g/cm^3). There is no space group imposed molecular symmetry with all atoms in the general space group positions.[6]

A needlelike crystal of dimensions 0.12 × 0.15 × 0.32 mm, enclosed in a capillary, was used in the data collection. The crystal was mounted on a Picker four-circle automatic diffractometer with c^* coincident with the diffractometer ϕ axis. The data were measured using Mo radiation (λ 0.7107 Å) diffracted from a highly oriented graphite (HOG) crystal in the Picker incident-beam monochromator. A total of 3645 reflections were measured including the symmetry-equivalent $hk0$ and $\bar{h}k0$ sets which were averaged. The data were measured out to 2θ of 40° using the θ-2θ scan technique with a scan speed of 1°/min and a scan range of 2.00° plus the $K\alpha_1$-$K\alpha_2$ separation. Backgrounds of 10 sec were measured before and after each scan.

The data were not corrected for absorption effects. The linear absorption coefficient for Mo Kα radiation is 6.0 cm^{-1}. In checks on equivalent reflections the maximum deviation in F_o which might be attributed to absorption was 4%. The structure factor errors were estimated as previously described.[7] In final refinements struc-

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[1] (a) P. T. Cheng, C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *Acta Crystallogr., Sect. B*, 27, 1904 (1971); (b) P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Inorg. Chem.*, 10, 2210 (1971); (c) C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *Chem. Commun.*, 426 (1967).

[2] W. Dreissing and H. Dietrich, *Acta Crystallogr., Sect. B*, 24, 108 (1968).

[3] C. A. Tolman and W. C. Seidel, to be submitted for publication.

[4] W. C. Seidel and C. A. Tolman, *Inorg. Chem.*, 9, 2354 (1970).

[5] C. A. Tolman, *J. Amer. Chem. Soc.*, 92, 2953, 2956 (1970).

[6] "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 99.

[7] L. J. Guggenberger, *Inorg. Chem.*, 7, 2260 (1968).

Table I. Final Positional and Thermal Parameters (×10^4) for $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.79456 (8)	0.05281 (12)	0.70692 (8)	35.1 (6)	56.1 (13)	29.4 (5)	8.0 (9)	−5.1 (5)	−3.4 (8)
P(1)	0.75531 (18)	0.15167 (24)	0.78794 (16)	31.6 (14)	47.1 (28)	26.9 (12)	0.6 (17)	−4.7 (10)	2.6 (14)
P(2)	0.72899 (18)	0.08658 (24)	0.61893 (16)	37.9 (15)	56.4 (30)	27.9 (11)	9.4 (16)	−0.2 (11)	−0.8 (15)
O(1)	0.6878 (5)	0.1062 (6)	0.8361 (4)	43 (4)	89 (8)	27 (3)	−22 (5)	2 (3)	9 (4)
O(2)	0.7252 (4)	0.2719 (6)	0.7632 (4)	47 (4)	58 (7)	28 (3)	−1 (4)	2 (3)	−1 (4)
O(3)	0.8112 (4)	0.1864 (6)	0.8500 (4)	34 (4)	101 (8)	30 (3)	15 (5)	−5 (3)	−16 (4)
O(4)	0.6571 (4)	0.1683 (6)	0.6243 (4)	33 (3)	72 (7)	24 (3)	7 (4)	2 (3)	−8 (4)
O(5)	0.7728 (5)	0.1360 (8)	0.5563 (4)	35 (4)	187 (12)	35 (3)	9 (6)	5 (3)	18 (5)
O(6)	0.6872 (6)	−0.0134 (6)	0.5800 (4)	124 (7)	38 (7)	42 (3)	18 (5)	−36 (4)	−7 (4)
N(1)	0.8371 (8)	−0.1810 (11)	0.8243 (8)	75 (7)	109 (15)	67 (7)	27 (9)	−20 (6)	8 (7)
C(1)	0.8673 (6)	−0.0585 (10)	0.6659 (5)	60 (6)	113 (13)	13 (4)	51 (8)	−17 (4)	−17 (6)
C(2)	0.8818 (7)	−0.0336 (9)	0.7371 (8)	59 (7)	29 (11)	50 (7)	2 (7)	8 (5)	32 (7)
C(3)	0.8574 (9)	−0.1116 (13)	0.7846 (9)	57 (9)	77 (17)	60 (9)	48 (11)	−38 (7)	−29 (9)
C(11)	0.6187 (7)	0.0569 (12)	0.8155 (6)	23 (6)	87 (14)	33 (5)	−13 (9)	2 (5)	−12 (7)
C(12)	0.5981 (8)	−0.0422 (12)	0.8467 (6)	51 (7)	77 (14)	39 (5)	−31 (9)	30 (5)	−12 (7)
C(13)	0.5249 (11)	−0.0834 (12)	0.8280 (9)	43 (9)	140 (18)	74 (8)	−30 (11)	23 (6)	−48 (9)
C(14)	0.4753 (9)	−0.0300 (20)	0.7819 (11)	28 (8)	236 (28)	80 (9)	−36 (12)	13 (7)	−46 (12)
C(15)	0.5008 (10)	0.0647 (18)	0.7520 (8)	33 (8)	246 (25)	46 (6)	−11 (11)	−1 (6)	−23 (11)
C(16)	0.5704 (10)	0.1145 (11)	0.7696 (7)	49 (7)	127 (15)	46 (6)	−1 (10)	−6 (6)	−9 (8)
C(17)	0.6531 (8)	−0.1023 (10)	0.8964 (7)	67 (7)	113 (14)	60 (6)	15 (8)	−3 (6)	48 (8)
C(21)	0.7119 (7)	0.3673 (11)	0.8043 (6)	30 (6)	61 (13)	19 (5)	32 (7)	4 (4)	−5 (6)
C(22)	0.7499 (7)	0.4656 (13)	0.7856 (7)	65 (7)	26 (16)	36 (5)	0 (10)	−17 (5)	5 (8)
C(23)	0.7239 (8)	0.5588 (13)	0.8245 (8)	56 (7)	65 (16)	51 (6)	−22 (9)	−12 (5)	−11 (8)
C(24)	0.6703 (9)	0.5481 (14)	0.8752 (8)	64 (8)	98 (18)	53 (6)	12 (10)	−4 (6)	−10 (9)
C(25)	0.6360 (8)	0.4486 (15)	0.8896 (7)	64 (7)	118 (15)	25 (5)	5 (10)	−1 (5)	−6 (9)
C(26)	0.6549 (8)	0.3560 (11)	0.8543 (7)	45 (7)	68 (14)	35 (5)	19 (8)	−1 (5)	−30 (7)
C(27)	0.8110 (8)	0.4680 (11)	0.7338 (7)	44 (7)	131 (15)	41 (5)	−5 (9)	37 (5)	8 (7)
C(31)	0.8894 (8)	0.1607 (11)	0.8551 (7)	18 (7)	88 (13)	36 (5)	9 (8)	0 (5)	−18 (7)
C(32)	0.9114 (9)	0.0867 (11)	0.9051 (7)	33 (8)	104 (15)	34 (5)	21 (8)	−29 (5)	−15 (7)
C(33)	0.9914 (11)	0.0620 (13)	0.9079 (8)	56 (9)	184 (17)	34 (7)	16 (12)	−11 (7)	14 (9)
C(34)	1.0421 (9)	0.1089 (15)	0.8656 (10)	50 (9)	201 (19)	47 (7)	−10 (11)	4 (7)	−22 (9)
C(35)	1.0183 (10)	0.1865 (13)	0.8164 (8)	62 (9)	155 (18)	53 (7)	−53 (10)	17 (6)	−18 (9)
C(36)	0.9393 (10)	0.2118 (11)	0.8108 (7)	46 (8)	95 (15)	51 (6)	−10 (9)	−3 (6)	−17 (7)
C(37)	0.8560 (8)	0.0316 (12)	0.9539 (7)	50 (7)	177 (15)	32 (6)	−31 (9)	25 (6)	29 (8)
C(41)	0.6031 (7)	0.2022 (11)	0.5726 (6)	24 (5)	79 (14)	22 (4)	9 (7)	−2 (4)	−4 (7)
C(42)	0.6126 (7)	0.3026 (10)	0.5421 (7)	41 (7)	63 (12)	37 (5)	−2 (8)	6 (5)	19 (6)
C(43)	0.5553 (8)	0.3323 (12)	0.4961 (7)	36 (7)	91 (16)	52 (6)	11 (9)	−1 (5)	18 (8)
C(44)	0.4931 (8)	0.2614 (14)	0.4807 (7)	22 (6)	133 (17)	42 (6)	18 (9)	−4 (5)	3 (8)
C(45)	0.4861 (7)	0.1646 (12)	0.5119 (8)	41 (7)	91 (15)	46 (6)	8 (8)	−5 (5)	7 (8)
C(46)	0.5426 (7)	0.1323 (10)	0.5587 (7)	37 (5)	53 (12)	43 (5)	3 (8)	−1 (5)	4 (7)
C(47)	0.6779 (8)	0.3806 (10)	0.5620 (8)	63 (8)	57 (11)	116 (9)	−38 (8)	−22 (7)	15 (8)
C(51)	0.8501 (10)	0.1637 (12)	0.5490 (9)	66 (9)	101 (16)	27 (6)	−17 (11)	−14 (7)	0 (8)
C(52)	0.8921 (11)	0.1348 (13)	0.4985 (10)	90 (12)	114 (17)	64 (8)	21 (12)	54 (9)	52 (10)
C(53)	0.9747 (10)	0.1700 (14)	0.5057 (10)	61 (10)	154 (18)	61 (8)	−25 (10)	−8 (7)	39 (10)
C(54)	0.9980 (10)	0.2266 (16)	0.5590 (13)	49 (10)	197 (22)	79 (10)	−32 (12)	10 (9)	35 (12)
C(55)	0.9449 (13)	0.2633 (14)	0.6160 (9)	83 (11)	196 (21)	52 (8)	−42 (13)	−7 (9)	−10 (10)
C(56)	0.8755 (10)	0.2274 (15)	0.6075 (9)	53 (10)	148 (19)	56 (7)	2 (11)	−7 (7)	47 (10)
C(57)	0.8678 (8)	0.0713 (11)	0.4427 (6)	129 (9)	96 (15)	27 (4)	−38 (9)	−15 (5)	−29 (7)

Group	Atoms[b]	x_c	y_c	z_c	ϕ	θ	ζ	B, Å^2
1	C(61)-C(67)	0.6807 (6)	−0.2195 (9)	0.6291 (5)	1.005 (10)	0.739 (8)	3.711 (12)	5.9 (3)
2	C(61)-C(67)	0.7255 (5)	−0.2291 (8)	0.5741 (5)	−1.053 (13)	5.261 (8)	6.494 (13)	4.4 (2)

[a] The estimated standard deviations here and in other tables are given in parentheses. The anisotropic thermal factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] x_c, y_c, z_c are the group centers in fractional coordinates and ϕ, θ, ζ are orientation angles for the groups in radians. Each group had a single isotropic temperature factor. The group description is described by C. Scheringer, *Acta Crystallogr.*, **16**, 546 (1963), and is similar to that used by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

Table II. Positional Parameters for the Rigid Groups[a]

Atom	x	y	z	Atom	x	y	z
C(61)	0.6918	−0.1148	0.6010	C(61)	0.6988	−0.1207	0.5818
C(62)	0.7294	−0.2068	0.5739	C(62)	0.6813	−0.2007	0.6300
C(63)	0.7183	−0.3115	0.6020	C(63)	0.7079	−0.3092	0.6223
C(64)	0.6696	−0.3242	0.6572	C(64)	0.7521	−0.3375	0.5664
C(65)	0.6320	−0.2322	0.6843	C(65)	0.7696	−0.2575	0.5181
C(66)	0.6431	−0.1275	0.6562	C(66)	0.7430	−0.1491	0.5258
C(67)	0.7819	−0.1931	0.5144	C(67)	0.6338	−0.1702	0.6904

[a] The left-hand set corresponds to group 1 in Table I (solid line in Figure 1A) and the right-hand set to group 2 (dashed line in Figure 1A).

ture factors with $F_o < 3\sigma(F_o)$ were considered "unobserved."[8]

Structure Solution and Refinement for $(C_2H_3CN)Ni[o\text{-}CH_3C_6H_4O)_3P]_2$. The structure was solved by symbolic addition techniques using the Fleischer, Dewar, and Stone program.[9] The statistical distribution of E's followed the centric theoretical distribution closely. Seven reflections were assigned symbolic phases, and the remaining phases of the largest E's were determined using the usual Σ_2 process. The −322, 054, and 349 reflections were used to assign the origin. The Ni and P atoms were located on the resultant E map, and they were used to phase an electron density map. The remaining nonhydrogen atoms were found in several steps. A model with all atoms included with isotropic temperature factors gave an R $(\Sigma|F_o|-|F_c|/\Sigma|F_o|)$ of 0.15.

It became clear very quickly that there was a definite disorder problem with one of the o-tolyl rings and a possible problem with a second ring. The disorder is an orientational disorder wherein the ring has two equivalent conformations rotated 180° with respect to

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(8) Computer programs used in addition to local programs were Prewitt's least-squares program SFLS5, the Busing-Levy error function program ORFFE, and the least-squares program ORFLS, a copy of which was received from Dr. G. D. Stucky.

(9) E. B. Fleischer, R. B. K. Dewar, and A. L. Stone, Abstracts, American Crystallographic Association Meeting, Georgia Institute of Technology, Atlanta, Ga., Jan 1967, No. A7.

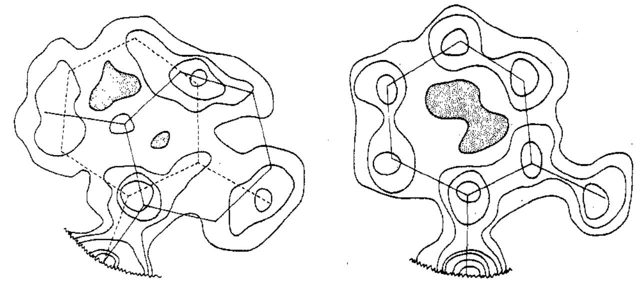

(A) (B)

Figure 1. (A) The electron density section through the disordered *o*-tolyl ring containing atoms C(61)–C(67). The refined positions of the two rigid groups used to account for the disorder are superimposed in this section. The shaded areas are regions of negative electron density. (B) The electron density section through the *o*-tolyl ring containing atoms C(51)–C(57).

the O–C ring bond. Figure 1A shows how the disorder was resolved for atoms C(61)–C(67). Figure 1A shows an electron density section through the plane of the ring. The *o*-tolyl ring was treated as a rigid body, and two rigid groups (one-half multiplicity) were varied in the least-squares process. The fit of the two rings is superimposed on the electron density map in Figure 1A. The rigid-body distances were fixed at C_{sp^2}–C_{sp^2} of 1.397 Å and C_{sp^2}–C_{sp^3} of 1.505 Å. Both conformations were assumed to be equally probable, although the refined-group temperature factors show a slight preference for group 2 (dashed in Figure 1A). Figure 1B shows the C(51)–C(57) plane which has some similarities to Figure 1A in the ring center and bond alternation. This ring was treated as having one conformation, but it probably has a small percentage of the second conformation as in Figure 1A. This is consistent with the spread in bond distances and angles observed for this ring. The other four *o*-tolyl rings were clearly ordered.

There was evidence for some of the hydrogen atom positions in an electron density difference map. Hydrogen atoms were included, but not refined, for the ordered rings in calculated positions with fixed isotropic temperature factors of 6.0 Å^2. The final refinements were done in three sections. The positional parameters and anisotropic thermal parameters were varied together in groups: (a) Ni, P(1), P(2), C(1)–C(3), N, O(1), C(11)–C(17); (b) O(2), O(3), C(21)–C(27), C(31)–C(37); (c) the remaining atoms and the two rigid groups. The final R values for 2182 observed reflections are 0.097 for R and 0.090 for R_w, $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Atomic scattering factors for the neutral atoms were used.[10] The real and imaginary parts[11] of the anomalous scattering of Ni were included in the calculations.

The final positional and thermal parameters are given in Table I. The disordered group atom positions are given in Table II, and the hydrogen atom positions in Table III. A list of observed and calculated structure factors (×10) is available.[12]

Cell and Intensity Data for $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$. Crystals are monoclinic with cell dimensions of $a = 11.812$ (4), $b = 9.823$ (4), $c = 18.337$ (9) Å, and $\beta = 109.50$ (9)°. These parameters resulted from the least-squares refinement of 13 reflections carefully centered on the diffractometer. The only systematic absence was for $h0l$, $l = 2n + 1$, characteristic of Pc or $P2/c$. The calculated density for two molecules per cell is 1.31 g/cm^3. As with the acrylonitrile complex, the density could not be measured experimentally. Either space group was possible for this molecule since the molecule could have $C_2(2)$ point symmetry required for $P2/c$. The refinement showed that the correct space group is Pc. There is no space group imposed molecular symmetry in Pc.

A prismatic crystal of dimensions 0.10 × 0.25 × 0.40 mm, enclosed in a capillary, was used in the data collection. The c^* axis was coincident with the diffractometer ϕ axis. The data collection was the same as with the acrylonitrile complex except that the data went out to 2θ of 45°, and the scan range was 1.3° plus the $K\alpha_1$–$K\alpha_2$ separation. A total of 2573 reflections was measured including the $hk0$ and $\bar{h}k0$ sets which were averaged.

Table III. Hydrogen Atom Positions for $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$

Atom	x	y	z
H(1)C(13)	0.5013	−0.1552	0.8492
H(2)C(14)	0.4251	−0.0636	0.7684
H(3)C(15)	0.4608	0.0983	0.7161
H(4)C(16)	0.5860	0.1894	0.7493
H(5)C(23)	0.7442	0.6367	0.8137
H(6)C(24)	0.6559	0.6196	0.9018
H(7)C(25)	0.5945	0.4472	0.9272
H(8)C(26)	0.6288	0.2818	0.8649
H(9)C(33)	1.0132	0.0022	0.9418
H(10)C(34)	1.1007	0.0917	0.8681
H(11)C(35)	1.0602	0.2241	0.7857
H(12)C(36)	0.9198	0.2715	0.7753
H(13)C(43)	0.5586	0.4096	0.4718
H(14)C(44)	0.4534	0.2848	0.4443
H(15)C(45)	0.4392	0.1144	0.5007
H(16)C(46)	0.5403	0.0577	0.5835
H(17)C(53)	1.0133	0.1520	0.4701
H(18)C(54)	1.0565	0.2540	0.5629
H(19)C(55)	0.9641	0.3091	0.6585
H(20)C(56)	0.8344	0.2489	0.6461

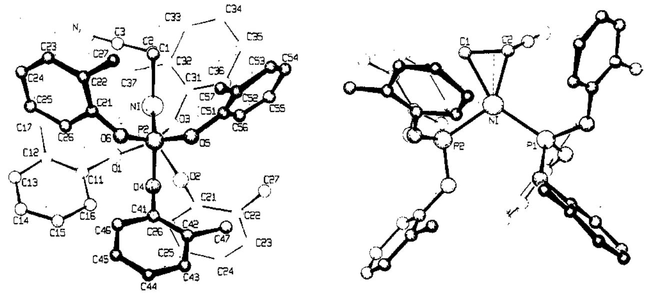
The data were not corrected for absorption effects. The linear absorption coefficient for Mo Kα radiation is 6.1 cm^{-1}. The structure factor errors were estimated as before, and the structure factors with $F_o < 2\sigma(F_o)$ were considered unobserved.

Structure Solution and Refinement for $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$. The Ni and P atoms were found using Patterson and Patterson superposition techniques. The remaining atoms were

Table IV. Structure Factor Comparison for Two Enantiomorphs in $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$[a]

Reflection	$F_o(hkl)$	$F_o(\overline{hkl})$	$F_c(hkl)$	$F_c(\overline{hkl})$
1,1,0	38.00	40.05	37.88	39.55
2,2,1	47.97	49.98	45.82	47.27
2,4,1	18.41	20.81	18.83	21.05
−2,2,3	21.21	18.41	18.59	16.57
−2,3,3	20.42	18.27	21.42	19.65
3,3,3	38.15	35.74	38.22	36.39
1,0,4	61.46	63.85	60.37	63.02
1,1,4	31.88	34.12	30.14	32.18
−4,3,5	40.09	43.34	40.69	42.93
2,3,5	15.17	11.39	13.64	11.33
−6,0,6	19.76	16.77	19.27	17.16
0,0,6	27.84	25.30	28.90	26.55
−2,3,7	19.83	16.83	19.19	17.26
−4,0,8	27.37	24.63	26.37	24.95
−2,0,16	13.18	16.34	13.51	14.77
−3,3,11	17.63	16.03	15.14	16.90

[a] The data are scaled differently from those in the structure factor list.



(A) (B)

Figure 2. Two views of the molecular structure of $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$. The left view is a side view of the PNiP plane on the right. The dotted line bisects the P–Ni–P angle.

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[10] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

[11] D. H. Templeton, "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 215.

[12] Tables of structure factors for both structures will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N. W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-499.

Table V. Final Positional and Thermal Parameters (×10⁴) for $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ [a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	0.08023 (18)	0.25	67.1 (18)	83.6 (22)	29.6 (8)	−6.4 (22)	15.6 (9)	−4.3 (15)
P(1)	0.15392 (41)	0.17613 (41)	0.32373 (26)	68.6 (44)	96.3 (54)	27.9 (17)	1.1 (41)	17.3 (23)	−1.4 (29)
P(2)	−0.15875 (37)	0.10922 (40)	0.27548 (25)	64.9 (39)	77.0 (50)	31.7 (18)	0.0 (38)	15.6 (22)	2.8 (26)
O(1)	0.2285 (8)	0.2727 (10)	0.2842 (6)	76 (11)	101 (13)	36 (4)	5 (10)	21 (6)	−3 (6)
O(2)	0.1430 (8)	0.2669 (9)	0.3941 (6)	72 (10)	78 (12)	27 (4)	−12 (9)	19 (5)	−2 (6)
O(3)	0.2673 (8)	0.0837 (10)	0.3754 (5)	86 (10)	88 (12)	30 (4)	6 (10)	15 (5)	2 (6)
O(4)	−0.2834 (8)	0.1157 (11)	0.2021 (6)	62 (10)	147 (17)	37 (4)	−37 (10)	3 (5)	−5 (7)
O(5)	−0.2034 (10)	−0.0056 (11)	0.3251 (6)	108 (12)	121 (15)	36 (4)	−4 (11)	27 (6)	−1 (7)
O(6)	−0.1691 (8)	0.2425 (10)	0.3217 (6)	66 (10)	93 (14)	45 (5)	6 (10)	17 (6)	−13 (7)
C(1)	0.0656 (18)	−0.0005 (22)	0.1726 (9)	114 (24)	207 (31)	32 (7)	−30 (23)	26 (10)	−25 (13)
C(2)	−0.0588 (19)	−0.0449 (19)	0.1558 (11)	156 (25)	151 (31)	45 (9)	−8 (23)	36 (12)	−23 (13)
C(11)	0.1703 (12)	0.3608 (15)	0.2242 (7)	56 (14)	128 (21)	21 (5)	12 (15)	9 (7)	11 (9)
C(12)	0.2061 (14)	0.3542 (19)	0.1580 (11)	65 (17)	151 (28)	38 (8)	−30 (18)	12 (10)	9 (13)
C(13)	0.1543 (18)	0.4515 (19)	0.1008 (10)	136 (21)	168 (28)	28 (8)	−26 (20)	18 (11)	26 (12)
C(14)	0.0778 (17)	0.5516 (22)	0.1091 (12)	125 (21)	243 (39)	58 (10)	32 (23)	25 (12)	64 (16)
C(15)	0.0437 (19)	0.5452 (20)	0.1734 (16)	139 (28)	99 (31)	83 (14)	9 (23)	17 (16)	12 (17)
C(16)	0.0906 (15)	0.4552 (17)	0.2319 (10)	119 (20)	74 (23)	34 (8)	11 (18)	14 (10)	14 (11)
C(17)	0.2922 (18)	0.2457 (22)	0.1456 (11)	141 (25)	168 (34)	57 (10)	25 (25)	63 (14)	−15 (16)
C(21)	0.2433 (13)	0.3230 (16)	0.4529 (9)	77 (15)	97 (21)	36 (8)	−13 (15)	27 (9)	−40 (11)
C(22)	0.2841 (16)	0.2587 (18)	0.5238 (10)	127 (21)	163 (26)	24 (7)	28 (20)	28 (11)	− 3 (12)
C(23)	0.3826 (18)	0.3258 (24)	0.5812 (9)	145 (24)	272 (38)	16 (7)	3 (26)	8 (11)	−26 (14)
C(24)	0.4309 (15)	0.4450 (24)	0.5639 (12)	54 (17)	203 (36)	56 (11)	−40 (20)	15 (11)	−80 (17)
C(25)	0.3832 (18)	0.5062 (20)	0.4930 (12)	147 (25)	157 (28)	42 (9)	−28 (23)	23 (13)	−22 (15)
C(26)	0.2896 (15)	0.4454 (17)	0.4369 (9)	114 (19)	101 (24)	39 (8)	−10 (17)	25 (10)	−41 (11)
C(27)	0.2249 (19)	0.1295 (18)	0.5427 (11)	209 (26)	120 (26)	50 (9)	−13 (22)	39 (13)	38 (13)
C(31)	0.3230 (14)	−0.0082 (17)	0.3419 (9)	63 (16)	146 (22)	29 (7)	23 (16)	27 (8)	10 (10)
C(32)	0.2861 (15)	−0.1438 (19)	0.3378 (10)	103 (19)	92 (25)	38 (8)	3 (18)	9 (10)	−10 (12)
C(33)	0.3520 (17)	−0.2355 (18)	0.3056 (9)	126 (21)	120 (26)	35 (7)	26 (21)	23 (11)	10 (11)
C(34)	0.4504 (18)	−0.1921 (24)	0.2880 (10)	140 (25)	180 (35)	35 (10)	75 (23)	23 (12)	−5 (14)
C(35)	0.4845 (18)	−0.0571 (25)	0.2975 (12)	100 (23)	200 (38)	65 (10)	48 (25)	37 (12)	34 (16)
C(36)	0.4219 (16)	0.0346 (17)	0.3258 (10)	98 (20)	114 (24)	42 (8)	21 (18)	28 (10)	−8 (11)
C(37)	0.1828 (16)	−0.1910 (16)	0.3635 (11)	114 (21)	90 (22)	91 (11)	−49 (18)	54 (13)	−6 (13)
C(41)	−0.2923 (13)	0.1760 (15)	0.1332 (8)	68 (15)	70 (20)	30 (7)	13 (15)	12 (9)	0 (10)
C(42)	−0.3838 (15)	0.1283 (19)	0.0662 (10)	83 (18)	197 (29)	40 (8)	20 (19)	9 (10)	−6 (13)
C(43)	−0.3920 (18)	0.1924 (21)	−0.0032 (10)	177 (25)	184 (30)	25 (8)	21 (23)	30 (11)	4 (13)
C(44)	−0.3220 (21)	0.2914 (25)	−0.0090 (13)	177 (27)	208 (37)	44 (12)	12 (26)	35 (16)	11 (18)
C(45)	−0.2337 (19)	0.3431 (21)	0.0567 (14)	127 (24)	139 (29)	76 (12)	−28 (22)	22 (14)	16 (16)
C(46)	−0.2185 (15)	0.2832 (19)	0.1286 (10)	93 (19)	153 (25)	45 (8)	30 (18)	21 (10)	33 (12)
C(47)	−0.4645 (17)	0.0101 (23)	0.0732 (12)	120 (21)	249 (32)	69 (11)	−128 (23)	−20 (12)	−27 (16)
C(51)	−0.1748 (21)	−0.1462 (22)	0.3248 (17)	132 (26)	155 (34)	66 (12)	−23 (26)	68 (15)	12 (20)
C(52)	−0.0959 (26)	−0.1944 (26)	0.3924 (20)	201 (38)	143 (38)	106 (19)	7 (29)	78 (23)	29 (22)
C(53)	−0.0723 (29)	−0.3397 (40)	0.3931 (24)	283 (47)	266 (72)	158 (26)	43 (45)	153 (32)	82 (35)
C(54)	−0.1293 (28)	−0.3988 (26)	0.3207 (25)	215 (38)	142 (35)	134 (21)	28 (30)	110 (25)	43 (26)
C(55)	−0.2077 (29)	−0.3450 (32)	0.2458 (15)	342 (44)	162 (38)	76 (13)	−109 (38)	89 (20)	−57 (22)
C(56)	−0.2313 (24)	−0.2164 (27)	0.2533 (17)	249 (36)	118 (33)	108 (18)	−76 (30)	106 (22)	−61 (20)
C(57)	−0.0444 (23)	−0.1136 (25)	0.4620 (14)	257 (35)	207 (39)	56 (11)	−25 (30)	12 (16)	−4 (17)
C(61)	−0.2733 (16)	0.2907 (17)	0.3355 (11)	136 (22)	87 (24)	56 (9)	−17 (18)	59 (12)	−6 (12)
C(62)	−0.2788 (24)	0.2843 (21)	0.4045 (16)	277 (40)	137 (30)	91 (14)	−88 (27)	99 (21)	−46 (18)
C(63)	−0.3849 (21)	0.3409 (22)	0.4213 (15)	143 (26)	157 (32)	108 (15)	13 (24)	82 (17)	−12 (18)
C(64)	−0.4677 (21)	0.4063 (25)	0.3599 (17)	156 (28)	175 (36)	106 (16)	−7 (28)	53 (18)	−56 (21)
C(65)	−0.4561 (19)	0.4108 (24)	0.2818 (13)	169 (31)	224 (36)	60 (11)	32 (28)	26 (14)	10 (17)
C(66)	−0.3588 (16)	0.3524 (16)	0.2719 (11)	73 (17)	104 (23)	70 (10)	43 (17)	10 (11)	−13 (13)
C(67)	−0.1859 (24)	0.2182 (21)	0.4736 (12)	301 (37)	195 (34)	29 (9)	82 (30)	−30 (15)	13 (15)

[a] The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

found in several steps using Fourier techniques. The R value with all nonhydrogen atoms in the model with isotropic thermal parameters was 0.147. The R was 0.118 with anisotropic thermal parameters for all atoms.

At this point electron density maps were calculated through all of the *o*-tolyl ring planes to check for orientational disorder, such as observed with the acrylonitrile complex (Figure 1). All the rings appeared to be ordered, although the spread in observed distances and angles might be attributed to small percentages of the second orientational conformation. Hydrogen atoms were included in their calculated positions with fixed isotropic thermal parameters of 6.0 Å².

A check was made here on whether the correct enantiomorph was chosen. The crystal was remounted, and all four members of the form were measured for 35 reflections which gave significant calculated differences for $F_c(hkl)$ and $F_c(\overline{hkl})$. Equivalent members of the form were averaged; for $C_s(m)$ point symmetry hkl is equivalent to $h\overline{k}l$ and $\overline{h}\overline{k}\overline{l}$ to $\overline{h}k\overline{l}$. Of the 35 reflections measured, 27 had $|F_o(hkl) - F_o(\overline{hkl})| > \sigma(F_o)$. Of these 27 reflections 26 indications were that the correct enantiomorph had been chosen. Some of these data are shown in Table IV; the −3,3,11 reflection was the only negative indication.

The final refinements were carried out in three groups. The positional and thermal factors were varied in the groups: (a) Ni, P(1), P(2), C(1), C(2), O(1)-O(6); (b) C(11)-C(17), C(31)-C(37), C(41)-C(47); (c) the remaining atoms. The same atom form factors

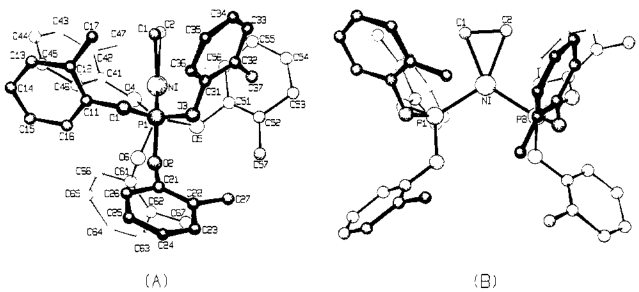

Figure 3. The molecular structure of $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ (same views as used in Figure 2).

were used as in the acrylonitrile complex. The final values for the 2059 observed data are 0.088 for R and 0.078 for R_w.

The final positional and thermal parameters are given in Table V. The coordinates of the hydrogen atoms are given in Table VI. A list of observed and calculated structure factors (×10) is available.[12]

Structure Descriptions

The crystal structures of $(C_2H_3CN)Ni[\textit{o}\text{-}CH_3C_6H_4O)_3P]_2$ and $(C_2H_4)Ni[(\textit{o}\text{-}CH_3C_6H_4O)_3P]_2$ both consist of the packing of discrete molecules separated by normal van der Waals forces. Generally, the molecular structures consist of an essentially trigonally coordinated Ni atom, assuming one coordination site for the olefin ligand, with the olefin ligands nearly in the PNiP plane. Two views of the molecular structure of the nickel-acrylonitrile complex illustrating the numbering system used here are given in Figure 2. The view on the right is normal to the PNiP plane, while the left view is a side view, in the P-P direction. The same views of the nickel-ethylene structure illustrating the numbering system used for that structure are shown in Figure 3. Neither structure has any idealized molecular symmetry.

Sets of interatomic distances and angles for $(C_2H_3CN)Ni[(\textit{o}\text{-}CH_3C_6H_4O)_3P]_2$ are given in Tables VII and VIII. The interatomic distances and angles for $(C_2H_4)Ni[(\textit{o}\text{-}CH_3C_6H_4O)_3P]_2$ are given in Tables IX and X. The most important comparison of distances and angles is the internal comparison between these two structures and that of $(C_2H_4)Ni[(C_6H_5)_3P]_2$. There are two independent determinations of the latter structure:[1,2] one [1a] involves a complete anisotropic refinement, while the other[2] refined only the nickel and phosphorus atoms anisotropically. The pertinent data for comparison of the three structures are summarized in Table XI. The recent structure determination of bis(ethylene)(tricyclohexylphosphine)nickel[13] also provides an interesting structural comparison (*vide infra*).

Table VI. Hydrogen Atom Positions for $(C_2H_4)Ni[(\textit{o}\text{-}CH_3C_6H_4O)_3P]_2$

Atom	x	y	z
H(1)C(13)	0.1813	0.4529	0.0533
H(2)C(14)	0.0471	0.6236	0.0678
H(3)C(15)	−0.0194	0.6133	0.1792
H(4)C(16)	0.0652	0.4539	0.2807
H(5)C(23)	0.4166	0.2830	0.6358
H(6)C(24)	0.5033	0.4827	0.6080
H(7)C(25)	0.4224	0.5961	0.4838
H(8)C(26)	0.2554	0.4944	0.3844
H(9)C(33)	0.3253	−0.3351	0.2960
H(10)C(34)	0.5004	−0.2572	0.2675
H(11)C(35)	0.5577	−0.0255	0.2825
H(12)C(36)	0.4492	0.1334	0.3341
H(13)C(43)	−0.4628	0.1594	−0.0527
H(14)C(44)	−0.3316	0.3292	−0.0637
H(15)C(45)	−0.1846	0.4268	0.0531
H(16)C(46)	−0.1528	0.3150	0.1764
H(17)C(53)	−0.0170	−0.3914	0.4437
H(18)C(54)	−0.1131	−0.4993	0.3183
H(19)C(55)	−0.2541	−0.3894	0.1986
H(20)C(56)	−0.2930	−0.1615	0.2018
H(21)C(63)	−0.3969	0.3349	0.4747
H(22)C(64)	−0.5419	0.4528	0.3675
H(23)C(65)	−0.5204	0.4605	0.2361
H(24)C(66)	−0.3538	0.3578	0.2188

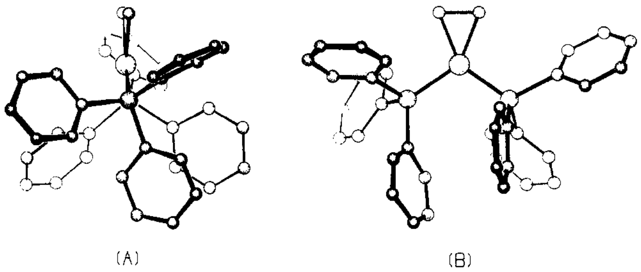

Figure 4. The molecular structure of $(C_2H_4)Ni[(C_6H_5)_3P]_2$ (same views as used in Figures 2 and 3).

There are few structures in the literature which have similar types of Ni(0)-P and Ni(0)-C bonds. Possible comparisons with Ni-P bonds are the Ni(0) value of 2.225 (3) Å in $(OC)_3NiPPh_2PPh_2Ni(CO)_3$,[14] the Ni(I) value of 2.190 (5) Å in $(OC)_2Ni(PPh_2)_2Ni(CO)_2$,[15] the Ni(II) values of 2.138 (2)-2.172 (9) Å in $(C_5H_5)Ni(PPh_3)C_6H_5$,[16] $(C_5H_5)Ni(PPh_3)C_6F_5$,[17] and $(C_5H_5)Ni(PPh_3)CF_3$,[18] 2.175 (4) Å in $Ni(C{\equiv}CPPh)_2(PEt_3)_2$,[19] 2.179 (4) Å in $(CH_2CMeCH_2)Ni(Ph_2P(CH_2)_2PPh_2)Br$,[20] 2.189 (6)-2.289 (5) Å in $Ni(CN)_2(PPh(CH_3)_2)_3$[21] and $Ni(CN)_2(PPh(OC_2H_5)_2)_3$,[22] 2.28 Å in $Ni(PPh_3)_2Cl_2$[23] and $[AsPh_4][Ni(PPh_3)I_3]$,[24] 2.315 (6) Å in $Ni(PPh_2C_2H_4OC_2H_4Ph_2P)Cl_2$,[25] and 2.333 (10) Å in $Ni(PPh_3)_2Br_2$.[26] Examples of Ni-C distances are 1.79 (1) and 1.80 (1) Å for carbonyl carbons in $(OC)_2Ni(PPh_2)_2Ni(CO)_2$,[15] 1.85 and 1.88 Å for average distances to cyano carbons in $Ni(CN)_2P(Ph(CH_3)_2)_3$[21] and $Ni(CN)_2(PPh(OC_2H_5)_2)_3$,[22] 1.87 (1) Å for acetylenic carbons in $Ni(C{\equiv}CPPh)_2(PEt_3)_2$,[19] 1.904 (7)-1.949 (29) Å for formally σ-bonded carbons in $(C_5H_5)Ni(PPh_3)X$ [$X = C_6F_5$,[17] C_6H_5,[16] or CF_3[18]], and 1.964 (12) Å for the σ bond in $(C_5H_5)Ni[C_2H_5C_2(OAc)_2]$.[27] Tuggle and Weaver[28] listed Ni-C distances observed in π-bond rings; the range is 1.94-2.20 Å. Since a good Ni(0) radius is not available, perhaps the best appraisal of the general comparison with literature values is that the Ni-P distances in the tri-*o*-tolyl phosphite complexes are among the shortest observed and the Ni-C distances are in the observed range; however, it is not possible to infer a bond order-bond length relationship from the observed data.

A comparison of C=C bond lengths in the different metal-olefin structures is given in Table XII. Structures included in the list are ordered at least with respect to the metal-olefin geometry with refinements based on three-dimensional data. The data in Table XII illustrate the relatively large errors involved in the light-atom positions in this type of structure.

The pertinent least-squares planes for the two structures determined here are given in Tables XIII and XIV. All rings appear to be acceptably planar within the errors of the

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(13) C. Kruger and Y. H. Tsay, *J. Organometal. Chem.*, 34, 387 (1972).

(14) R. H. B. Mais, P. G. Owston, D. T. Thompson, and A. M. Wood, *J. Chem. Soc. A*, 1744 (1967).

(15) J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc. A*, 1867 (1970).

(16) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 266 (1969).

(17) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968).

(18) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 161 (1970).

(19) G. R. Davies, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1750 (1967).

(20) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 206 (1970).

(21) J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 8, 1090 (1969).

(22) J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 8, 1084 (1969).

(23) G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).

(24) R. P. Taylor, D. H. Templeton, A. Zalkin, and W. D. Horrocks, *Inorg. Chem.*, 7, 2629 (1968).

(25) P. T. Greene and L. Sacconi, *J. Chem. Soc. A*, 866 (1970).

(26) J. A. J. Jarvis, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1473 (1968).

(27) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 2, 713 (1963).

(28) R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, 10, 1504 (1971).

Table VII. Selected Interatomic Distances for $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ (Å)[a]

Bonding Distances

Ni-P(1)	2.121 (4)	Benzene C(sp^2)-C(sp^2)	
Ni-P(2)	2.096 (4)	C(11)-C(12)	1.40 (1)
Ni-C(1)	2.016 (10)	C(12)-C(13)	1.39 (2)
Ni-C(2)	1.911 (12)	C(13)-C(14)	1.39 (2)
C(1)-C(2)	1.46 (2)	C(14)-C(15)	1.36 (2)
C(2)-C(3)	1.40 (2)	C(15)-C(16)	1.37 (2)
C(3)-N	1.20 (2)	C(16)-C(11)	1.40 (2)
P(1)-O(1)	1.61 (1)	C(21)-C(22)	1.41 (2)
P(1)-O(2)	1.62 (1)	C(22)-C(23)	1.44 (2)
P(1)-O(3)	1.60 (1)	C(23)-C(24)	1.38 (2)
P(2)-O(4)	1.59 (1)	C(24)-C(25)	1.37 (2)
P(2)-O(5)	1.58 (1)	C(25)-C(26)	1.36 (2)
P(2)-O(6)	1.60 (1)	C(26)-C(21)	1.41 (1)
	1.60 (1)	C(31)-C(32)	1.38 (2)
O(1)-C(11)	1.38 (1)	C(32)-C(33)	1.40 (2)
O(2)-C(21)	1.43 (1)	C(33)-C(34)	1.34 (2)
O(3)-C(31)	1.38 (2)	C(34)-C(35)	1.41 (2)
O(4)-C(41)	1.43 (1)	C(35)-C(36)	1.39 (2)
O(5)-C(51)	1.38 (2)*	C(36)-C(31)	1.38 (2)
O(6)-C(61)	1.31 (2)*	C(41)-C(42)	1.37 (1)
	1.40 (1)	C(42)-C(43)	1.38 (2)
Benzene C(sp^2)-C(sp^3)		C(43)-C(44)	1.40 (2)
C(12)-C(17)	1.53 (2)	C(44)-C(45)	1.33 (2)
C(22)-C(27)	1.48 (2)	C(45)-C(46)	1.38 (2)
C(32)-C(37)	1.52 (2)	C(46)-C(41)	1.36 (2)
C(42)-C(47)	1.51 (2)	C(51)-C(52)	1.29 (3)*
C(52)-C(57)	1.40 (2)*	C(52)-C(53)	1.48 (3)*
	1.51 (1)	C(53)-C(54)	1.31 (3)*
		C(54)-C(55)	1.52 (3)*
		C(55)-C(56)	1.27 (3)*
		C(56)-C(51)	1.45 (2)*
			1.383 (5)

Nonbonding Distances

Ni-C(3)	2.72 (2)	O(6)-C(41)	2.98 (2)
P(1)-C(11)	2.67 (1)	O(6)-C(46)	3.06 (2)
P(1)-C(21)	2.73 (1)	O(4)-O(2)	3.22 (1)
P(1)-C(31)	2.64 (1)	O(4)-C(16)	3.33 (2)
P(2)-C(41)	2.72 (1)	O(3)-C(21)	2.91 (1)
P(2)-C(51)	2.68 (2)	O(2)-C(11)	3.35 (2)
P(2)-C(61)	2.66 (2)	O(2)-C(16)	3.27 (2)
P(1)-C(2)	3.29 (1)	O(1)-C(21)	3.25 (2)
P(2)-C(1)	3.08 (1)	O(1)-C(26)	3.09 (2)
O(1)-O(2)	2.56 (1)	C(2)-C(31)	3.31 (2)
O(1)-O(3)	2.34 (1)	P(2)-H(56)	2.71
O(2)-O(3)	2.47 (1)	O(6)-H(46)	2.66
O(4)-O(5)	2.45 (1)	O(4)-H(16)	2.79
O(4)-O(6)	2.42 (1)	O(2)-H(16)	2.60
O(5)-O(6)	2.38 (1)	O(1)-H(26)	2.42
O(5)-C(41)	3.04 (2)	C(11)-H(26)	2.89

[a] Mean distances are given where meaningful. The estimated error of the mean was calculated according to $[\Sigma_i^n(d_i - \bar{d})^2/n(n-1)]^{1/2}$ where d_i and $\bar{d}$ are the distance and mean distance, respectively. The values with asterisks were not included in the averages because of the possibility of disordered conformations (see text).

Table VIII. Selected Interatomic Angles for $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ (deg)[a]

P(1)-Ni-P(2)	110.3 (1)	C(11)-C(12)-C(13)	115.0 (14)
P(1)-Ni-C(1)	152.7 (3)	C(12)-C(13)-C(14)	122.9 (16)
P(1)-Ni-C(2)	109.2 (5)	C(13)-C(14)-C(15)	118.4 (16)
P(2)-Ni-C(1)	97.0 (3)	C(14)-C(15)-C(16)	122.7 (17)
P(2)-Ni-C(2)	140.4 (5)	C(15)-C(16)-C(11)	116.5 (14)
C(1)-Ni-C(2)	43.5 (4)	C(16)-C(11)-C(12)	124.1 (12)
Ni-C(1)-C(2)	64.4 (6)	C(11)-C(12)-C(17)	122.2 (13)
Ni-C(2)-C(1)	72.1 (7)	C(13)-C(12)-C(17)	122.8 (14)
C(1)-C(2)-C(3)	117.6 (11)		120.6 (12)
C(2)-C(3)-N	178.1 (17)	C(21)-C(22)-C(23)	111.6 (12)
Ni-P(1)-O(1)	119.9 (3)	C(22)-C(23)-C(24)	122.2 (14)
Ni-P(1)-O(2)	112.4 (3)	C(23)-C(24)-C(25)	121.9 (15)
Ni-P(1)-O(3)	122.3 (3)	C(24)-C(25)-C(26)	120.4 (13)
Ni-P(2)-O(4)	118.1 (3)	C(25)-C(26)-C(21)	117.1 (12)
Ni-P(2)-O(5)	118.1 (3)	C(26)-C(21)-C(22)	126.7 (12)
Ni-P(2)-O(6)	118.9 (3)	C(21)-C(22)-C(27)	122.4 (14)
	118.3 (13)	C(23)-C(22)-C(27)	125.9 (14)
O(1)-P(1)-O(2)	105.0 (4)		121.0 (17)
O(1)-P(1)-O(3)	93.5 (4)	C(31)-C(32)-C(33)	114.9 (14)
O(2)-P(1)-O(3)	100.4 (4)	C(32)-C(33)-C(34)	121.9 (15)
O(4)-P(2)-O(5)	101.5 (5)	C(33)-C(34)-C(35)	122.0 (16)
O(4)-P(2)-O(6)	99.3 (5)	C(34)-C(35)-C(36)	118.2 (15)
O(5)-P(2)-O(6)	97.1 (5)	C(35)-C(36)-C(31)	117.6 (14)
	99.5 (16)	C(36)-C(31)-C(32)	125.4 (13)
P(1)-O(1)-C(11)	126.4 (7)	C(31)-C(32)-C(37)	125.0 (13)
P(1)-O(2)-C(21)	127.2 (7)	C(33)-C(32)-C(37)	120.1 (15)
P(1)-O(3)-C(31)	124.4 (8)		120.6 (13)
P(2)-O(4)-C(41)	128.7 (7)	C(41)-C(42)-C(43)	115.8 (12)
P(2)-O(5)-C(51)	130.3 (9)*	C(42)-C(43)-C(44)	121.1 (12)
P(2)-O(6)-C(61)	131.9 (9)*	C(43)-C(44)-C(45)	120.9 (13)
	126.7 (9)	C(44)-C(45)-C(46)	119.5 (13)
O(1)-C(11)-C(12)	117.5 (13)	C(45)-C(46)-C(41)	118.7 (12)
O(2)-C(21)-C(22)	116.7 (12)	C(46)-C(41)-C(42)	123.9 (11)
O(3)-C(31)-C(32)	116.8 (13)	C(41)-C(42)-C(47)	122.2 (13)
O(4)-C(41)-C(42)	119.4 (12)	C(43)-C(42)-C(47)	121.8 (12)
O(5)-C(51)-C(52)	124.5 (17)*		120.5 (9)
O(6)-C(61)-C(62)	131.9 (14)*	C(51)-C(52)-C(53)	113.1 (18)
	117.6 (6)	C(52)-C(53)-C(54)	120.2 (18)
O(1)-C(11)-C(16)	118.1 (13)	C(53)-C(54)-C(55)	124.6 (17)
O(2)-C(21)-C(26)	116.2 (11)	C(54)-C(55)-C(56)	111.7 (17)
O(3)-C(31)-C(36)	117.8 (13)	C(55)-C(56)-C(51)	123.6 (18)
O(4)-C(41)-C(46)	116.6 (12)	C(56)-C(51)-C(52)	126.7 (17)
O(5)-C(51)-C(56)	108.8 (15)*	C(51)-C(52)-C(57)	126.6 (18)
O(6)-C(61)-C(66)	107.8 (13)*	C(53)-C(52)-C(57)	120.2 (18)
	117.2 (5)		120.8 (20)

[a] Footnote to Table VII applies here.

measurements. The dihedral angles between the Ni-P and Ni-olefin planes are given in Table XI. The orientations of the *o*-tolyl rings (shown in Figures 2 and 3) result from the usual packing requirements (intra- and intermolecular); individual dihedral angles between *o*-tolyl rings do not appear to be of any particular significance.

The intermolecular contacts were calculated for both structures. The shortest contacts in the $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ structure are 3.49 Å for C-C, 2.82 Å for C-H, 2.72 Å for N-H, and 2.36 Å for H-H. The shortest contacts in the $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ structure are 2.70 Å for C-H, 2.63 Å for O-H, and 2.30 Å for H-H; there are no C-C or C-O contacts less than 3.5 Å.

Discussion

The most interesting point here is the comparison of the $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$, $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$, and $(C_2H_4)Ni[(C_6H_5)_3P]_2$ structures and the implications with respect to the Ni-olefin bonding. The structural differences can be discussed in terms of steric and electronic effects. The steric-electronic separation is not, of course, straightforward since the two are frequently interdependent. However, some of the differences appear to fall naturally into one or the other category.

Two views of the molecular structure of $(C_2H_4)Ni[(C_6H_5)_3P]_2$ are shown in Figure 4. The coordinates for this drawing were taken from ref 2. Figures 2-4 then show identical views of the three Ni-olefin structures for comparison purposes. The rotations of the phosphorus tetrahedra (left views in Figures 2-4) appear to arise from steric effects. The steric constraints are the smallest in the $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ structure (Figure 3); the phosphorus tetrahedra are able to approach the eclipsed conformation.

In the acrylonitrile complex (Figure 2) the phosphorus

Table IX. Selected Interatomic Distances for $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ (Å)[a]

Bonding Distances

Ni–P(1)	2.093 (5)
Ni–P(2)	2.098 (4)
	2.095 (2)
Ni–C(1)	1.99 (2)
Ni–C(2)	2.04 (2)
	2.02 (2)
C(1)–C(2)	1.46 (2)
P(1)–O(1)	1.62 (1)
P(1)–O(2)	1.61 (1)
P(1)–O(3)	1.63 (1)
P(2)–O(4)	1.63 (1)
P(2)–O(5)	1.64 (1)
P(2)–O(6)	1.59 (1)
	1.62 (1)
O(1)–C(11)	1.39 (2)
O(2)–C(21)	1.42 (2)
O(3)–C(31)	1.38 (2)
O(4)–C(41)	1.37 (2)
O(5)–C(51)	1.42 (2)
O(6)–C(61)	1.42 (2)
	1.40 (1)
Benzene C(sp^2)–C(sp^3)	
C(12)–C(17)	1.54 (2)
C(22)–C(27)	1.54 (2)
C(32)–C(37)	1.52 (2)
C(42)–C(47)	1.53 (2)
C(52)–C(57)	1.45 (3)
C(62)–C(67)	1.52 (3)
	1.52 (1)

Benzene C(sp^2)–C(sp^2)	
C(11)–C(12)	1.41 (2)
C(12)–C(13)	1.40 (2)
C(13)–C(14)	1.38 (2)
C(14)–C(15)	1.37 (3)
C(15)–C(16)	1.36 (2)
C(16)–C(11)	1.36 (2)
C(21)–C(22)	1.38 (2)
C(22)–C(23)	1.44 (2)
C(23)–C(24)	1.38 (2)
C(24)–C(25)	1.37 (3)
C(25)–C(26)	1.37 (2)
C(26)–C(21)	1.39 (2)
C(31)–C(32)	1.40 (2)
C(32)–C(33)	1.44 (2)
C(33)–C(34)	1.37 (2)
C(34)–C(35)	1.38 (3)
C(35)–C(36)	1.37 (2)
C(36)–C(31)	1.36 (2)
C(41)–C(42)	1.42 (2)
C(42)–C(43)	1.39 (2)
C(43)–C(44)	1.30 (2)
C(44)–C(45)	1.40 (2)
C(45)–C(46)	1.40 (2)
C(46)–C(41)	1.39 (2)
C(51)–C(52)	1.36 (3)
C(52)–C(53)	1.45 (4)
C(53)–C(54)	1.40 (4)
C(54)–C(55)	1.48 (4)
C(55)–C(56)	1.31 (4)
C(56)–C(51)	1.43 (3)
C(61)–C(62)	1.29 (2)
C(62)–C(63)	1.49 (3)
C(63)–C(64)	1.38 (3)
C(64)–C(65)	1.48 (3)
C(65)–C(66)	1.35 (2)
C(66)–C(61)	1.40 (2)

Nonbonding Distances

P(1)–C(11)	2.63 (2)	O(1)–C(26)	3.14 (2)
P(1)–C(21)	2.67 (2)	O(1)–C(21)	3.08 (2)
P(1)–C(31)	2.63 (2)	O(1)–C(31)	3.03 (2)
P(2)–C(41)	2.64 (2)	O(1)–C(36)	3.18 (2)
P(2)–C(51)	2.70 (2)	O(3)–C(27)	3.30 (2)
P(2)–C(61)	2.69 (2)	O(3)–C(22)	3.17 (2)
P(1)–C(1)	3.14 (2)	O(3)–C(21)	2.81 (2)
P(2)–C(2)	3.20 (2)	O(4)–C(61)	2.96 (2)
O(1)–O(2)	2.54 (1)	O(4)–C(66)	2.93 (2)
O(1)–O(3)	2.44 (1)	O(5)–C(61)	3.05 (2)
O(2)–O(3)	2.42 (1)	O(6)–C(41)	3.34 (2)
O(4)–O(5)	2.45 (1)	C(41)–H(24)C(66)	2.64
O(4)–O(6)	2.49 (1)	C(46)–H(24)C(66)	2.76
O(5)–O(6)	2.48 (1)		

[a] The error of the mean was estimated as in the footnote to Table VII.

Table X. Selected Interatomic Angles for $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ (deg)[a]

P(1)–Ni–P(2)	116.3 (2)
C(1)–Ni–C(2)	42.5 (6)
P(1)–Ni–C(1)	100.3 (6)
P(2)–Ni–C(2)	101.1 (6)
	100.7 (4)
P(1)–Ni–C(2)	142.5 (6)
P(2)–Ni–C(1)	143.2 (6)
	142.8 (3)
Ni–C(1)–C(2)	70.6 (10)
Ni–C(2)–C(1)	67.0 (10)
	68.8 (18)
Ni–P(1)–O(1)	117.4 (4)
Ni–P(1)–O(2)	118.9 (4)
Ni–P(1)–O(3)	119.5 (4)
Ni–P(2)–O(4)	116.7 (4)
Ni–P(2)–O(5)	120.4 (4)
Ni–P(2)–O(6)	117.7 (4)
	118.4 (4)
O(1)–P(1)–O(2)	103.6 (5)
O(1)–P(1)–O(3)	97.0 (5)
O(2)–P(1)–O(3)	96.4 (5)
O(4)–P(2)–O(5)	96.6 (5)
O(4)–P(2)–O(6)	101.5 (5)
O(5)–P(2)–O(6)	100.1 (5)
	99.2 (12)
P(1)–O(1)–C(11)	121.3 (8)
P(1)–O(2)–C(21)	123.6 (8)
P(1)–O(3)–C(31)	121.8 (8)
P(2)–O(4)–C(41)	123.3 (8)
P(2)–O(5)–C(51)	123.0 (11)
P(2)–O(6)–C(61)	126.7 (8)
	123.3 (8)
O(1)–C(11)–C(12)	116.2 (12)
O(2)–C(21)–C(22)	118.6 (13)
O(3)–C(31)–C(32)	117.5 (13)
O(4)–C(41)–C(42)	117.3 (12)
O(5)–C(51)–C(52)	115.2 (22)
O(6)–C(61)–C(62)	119.4 (16)
	117.4 (6)
O(1)–C(11)–C(16)	121.2 (12)
O(2)–C(21)–C(26)	117.6 (13)
O(3)–C(31)–C(36)	117.8 (13)
O(4)–C(41)–C(46)	121.9 (13)
O(5)–C(51)–C(56)	115.6 (21)
O(6)–C(61)–C(66)	115.0 (14)
	118.2 (12)

C(11)–C(12)–C(13)	115.5 (16)
C(12)–C(13)–C(14)	122.9 (17)
C(13)–C(14)–C(15)	117.1 (19)
C(14)–C(15)–C(16)	123.4 (21)
C(15)–C(16)–C(11)	118.4 (17)
C(16)–C(11)–C(12)	122.4 (14)
C(11)–C(12)–C(17)	124.0 (16)
C(13)–C(12)–C(17)	120.5 (17)
	120.5 (11)
C(21)–C(22)–C(23)	114.9 (16)
C(22)–C(23)–C(24)	120.9 (17)
C(23)–C(24)–C(25)	121.2 (16)
C(24)–C(25)–C(26)	119.5 (18)
C(25)–C(26)–C(21)	119.6 (16)
C(26)–C(21)–C(22)	123.7 (15)
C(21)–C(22)–C(27)	123.1 (16)
C(23)–C(22)–C(27)	121.9 (17)
	120.6 (10)
C(31)–C(32)–C(33)	114.6 (16)
C(32)–C(33)–C(34)	121.2 (18)
C(33)–C(34)–C(35)	120.2 (18)
C(34)–C(35)–C(36)	120.4 (20)
C(35)–C(36)–C(31)	119.2 (17)
C(36)–C(31)–C(32)	123.9 (15)
C(31)–C(32)–C(37)	122.9 (15)
C(33)–C(32)–C(37)	122.4 (16)
	120.6 (10)
C(41)–C(42)–C(43)	116.2 (17)
C(42)–C(43)–C(44)	124.0 (19)
C(43)–C(44)–C(45)	120.7 (21)
C(44)–C(45)–C(46)	118.9 (19)
C(45)–C(46)–C(41)	119.3 (16)
C(46)–C(41)–C(42)	120.7 (15)
C(41)–C(42)–C(47)	119.5 (16)
C(43)–C(42)–C(47)	124.2 (17)
	120.4 (9)
C(51)–C(52)–C(53)	114.8 (31)
C(52)–C(53)–C(54)	111.7 (32)
C(53)–C(54)–C(55)	128.9 (27)
C(54)–C(55)–C(56)	112.4 (27)
C(55)–C(56)–C(51)	122.7 (30)
C(56)–C(51)–C(52)	129.2 (24)
C(51)–C(52)–C(57)	128.4 (25)
C(53)–C(52)–C(57)	116.5 (34)
	120.6 (27)
C(61)–C(62)–C(63)	120.3 (25)
C(62)–C(63)–C(64)	114.8 (22)
C(63)–C(64)–C(65)	121.5 (21)
C(64)–C(65)–C(66)	119.6 (20)
C(65)–C(66)–C(61)	120.3 (20)
C(66)–C(61)–C(62)	123.4 (20)
C(61)–C(62)–C(67)	125.5 (24)
C(63)–C(62)–C(67)	114.2 (21)
	119.9 (14)

[a] The error of the mean was estimated as in Table VII.

tetrahedra are further rotated, apparently because of contacts involving the CN olefin substituent. The steric constraints of the triphenylphosphine ligand force the staggered phosphorus tetrahedron in the $(C_2H_4)Ni[(C_6H_5)_3P]_2$ structure (Figure 4). Thus for these complexes the steric requirements of *o*-tolyl phosphite ligands appear to be less than triphenylphosphine. The P–O and O–C distances (Table XI) are similar to distances frequently found in organophosphine and orthophosphate esters.[29] It is common in these ligands to have the M–P–O angles larger than tetrahedral and the O–P–O angles less than tetrahedral.

The packing of atoms C(61)–C(67) in the acrylonitrile complex is interesting; this is the disordered *o*-tolyl ring (*vide supra*). There were noticeably fewer short contacts (<3.50 Å) between both conformations and neighboring atoms. There are no strong packing potentials to favor one conformation which makes the 180° orientation disorder understandable for this ring.

In the Ni(0)- and Pt(0)-olefin complexes (Table XII) the olefin is nearly, but not exactly, in the PMP plane. The dihedral angles between the PMP and M-olefin planes vary between 1.30° (olefin is C_2H_4[1b]) and 12.3° (olefin is $C_2(Cl)_4$, footnote *h* in Table XII). The olefin position is in a shallow potential and steric effects may be enough to account for these twists, although electronic effects cannot be excluded completely. The previously observed metal-olefin geometries have involved an actual twist of the two

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(29) D. E. C. Corbridge, *Top. Phosphorus Chem.*, 3, 212 (1966).

Table XI. Comparison of Ni-Olefin Structures

	$(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$	$(C_2H_4)Ni[o\text{-}CH_3C_6H_4O)_3P]_2$ [2]	$(C_2H_4)Ni[(C_6H_5)_3P]_2$	
			A[a]	B[b]
Ni-P, Å	2.121 (4) (CH_2 trans) 2.096 (4) (CHCN trans)	2.095 (2)	2.152 (5)	2.16
Ni-C, Å	2.016 (10) (CH_2) 1.911 (12) (CHCN)	2.02 (2)	1.99 (1)	1.94
C=C, Å	1.46 (2)	1.46 (2)	1.43 (1)	1.41
P-Ni-P, deg	110.3 (1)	116.3 (2)	110.5 (2)	111
C-Ni-C, deg	43.5 (4)	42.5 (6)	42.1 (5)	43
Ni-C-C, deg	64.4 (6) (CH_2) 72.1 (7) (CHCN)	68.8 (18)	68.9 (8)	
(CNiC)-(PNiP) dihedral angle, deg	3.9 (1)	6.6 (11)	5.0	10
		Ligand Data		
P-O(C),[c] Å	1.60 (1)	1.62 (1)	1.84 (1)	1.83
O-C, Å	1.40 (1)	1.40 (1)		
Ni-P-O(C), deg	118.3 (13)	118.4 (4)	116 (2)	116
O(C)-P-O(C), deg	99.5 (16)	99.2 (12)	103 (1)	103

[a] Reference 1a. [b] Reference 2. [c] C in parentheses refers to carbon in place of oxygen for the triphenylphosphine ligand.

Table XII. Olefin Double-Bond Lengths (Å)

Metal		C=C	Olefin substituents if not hydrogen
Ni(0)	$(C_2H_4)_2Ni[(C_6H_{11})_3P]$[a]	1.401 (14)	
	$(C_2H_4)Ni[(C_6H_5)_3P]_2$	1.41[b]	
		1.43 (1)[c]	
	$(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$[d]	1.46 (2)	
	$(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$[d]	1.46 (2)	1 CN
	$[C_2(CN)_4]Ni(C_4H_9NC)_2$[e]	1.476 (5)	4 CN's
Pt(0)	$[Cl_2CC(CN)_2]Pt[(C_6H_5)_3P]_2$[f]	1.42 (3)	2 Cl's, 2 CN's
	$(C_2H_4)Pt[(C_6H_5)_3P]_2$[c]	1.43	
	$[C_2(CN)_4]Pt[(C_6H_5)_3P]_2$[g]	1.49 (5)	4 CN's
	$[C_2(Cl)_4]Pt[(C_6H_5)_3P]_2$[h]	1.62 (3)	4 Cl's
Pt(II)	$(C_2H_4)KPtCl_3 \cdot H_2O$	1.37 (3)[i]	
		1.354 (15)[j]	
	$[C_2H_2(CH_3)_2]PtCl_2$(phenethylamine)[k]	1.36 (6)	2 CH_3's
	$PtCl(OCH_3)$(dicyclopentadiene)[l]	1.37	Complex
	$[(C_4H_{12}N_2)PtCl_3]Cl \cdot {}^1/_2H_2O$[m]	1.416 (12)	2 CH_2NH_3's
	$(C_{10}H_{14}O_3)PtCl_2$[n]	1.42 (3)	Complex
Rh(I)	$(C_2H_4)(C_2F_4)Rh(C_5H_5)$[o]	1.358 (9)	
		1.405 (7)	4 F's
	$(C_2H_4)(C_2F_4)Rh(C_5H_7O_2)$[p]	1.40 (2)	4 F's
		1.42 (2)	
	$(C_2H_4)_2Rh(C_5H_7O_2)$[p]	1.41 (3)	
	$(C_2F_4)Rh[(C_6H_5)_3P]_2Cl$[q]	1.41	4 F's
Ir(I)	$[C_2H_2(CN)_2]IrH(CO)[(C_6H_5)_3P]_2$[r]	1.431 (20)	2 CN's
	$[C_2(CN)_4]IrBr(CO)[(C_6H_5)_3P]_2$[r]	1.506 (15)	4 CN's
	$[C_2(CN)_4]Ir(C_6N_4H)(CO)[(C_6H_5)_3P]_2$[s]	1.526 (12)	4 CN's
Fe(0)	$(C_2H_3CN)Fe(CO)_4$[t]	1.40 (2)	1 CN
	$[C_2H_2(CO_2H)_2]Fe(CO)_4$[u]	1.40 (5)	2 CO_2H's
	$[o\text{-}CH_2{=}CH(C_6H_4)PPh_2]_2Fe(CO)_2$[v]	1.45 (2)	Complex

[a] Reference 13. [b] Reference 2. [c] Reference 1. [d] This work. [e] J. K. Stalick and J. A. Ibers, *J. Amer. Chem. Soc.*, 92, 5333 (1970). [f] A. McAdam, J. N. Francis, and J. A. Ibers, *J. Organometal. Chem.*, 29, 149 (1971). [g] G. Bombieri, E. Forsellini, C. Panattoni, R. Graziani, and G. Bandoli, *J. Chem. Soc.*, 1313 (1970). [h] J. N. Francis, A. McAdam, and J. A. Ibers, *J. Organometal. Chem.*, **29**, 131 (1971). [i] J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *Acta Crystallogr., Sect. B*, **27**, 366 (1971). [j] W. C. Hamilton, K. A. Klanderman, and R. Spratley, *Acta Crystallogr., Sect. A*, **25**, S172 (1969). [k] E. Benedetti, P. Corradini, and C. Pedone, *J. Organometal. Chem.*, **18**, 203 (1969). [l] W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966). [m] R. Spagna and L. Zambonelli, *J. Chem. Soc. A*, 2544 (1971). [n] R. Mason and G. B. Robertson, *J. Chem. Soc. A*, 492 (1969). [o] Reference 30. [p] J. A. Evans and D. R. Russell, *Chem. Commun.*, 197 (1971). [q] P. B. Hitchcock, M. McPartlin, and R. Mason, *ibid.*, 1367 (1969). [r] L. M. Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, **47**, 84 (1969). [s] J. S. Ricci and J. A. Ibers, *J. Amer. Chem. Soc.*, **93**, 2391 (1971). [t] Reference 31. [u] C. Pedone and A. Sirigu, *Inorg. Chem.*, **7**, 2614 (1968). [v] M. A. Bennett, G. B. Robertson, I. B. Tomkins, and P. O. Whimp, *Chem. Commun.*, 341 (1971).

planes as in the (*o*-tolyl phosphite)nickel-ethylene complex (Figure 3A); however, in the acrylonitrile complex (Figure 2A) this plane is not twisted but folded by about 4° with respect to the PNiP plane. This is also evident from plane 1 in Table XIII where both C(1) and C(2) are displaced 0.07 Å on the same side of the plane, away from the acrylonitrile-ligand interactions. Hence, this may be a steric effect.

The P-Ni-P angle of 116.3 (2)° in $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$ is distinctly larger than the others in Table XI. This is hard to rationalize in terms of a steric effect; the O(2)-O(6) distance is 3.48 (1) Å. Perhaps it arises electronically from the increased Ni-P bonding in this complex (*vide infra*).

It is clear from Figure 2 that the CN substituent on the olefin in the acrylonitrile complex is bent back on coordination to Ni. The dihedral angle between the NiC(1)C(2) plane and the C(2)C(3)C(1) plane is 103.2°. This angle is 90° for planar olefin geometry. The expected angle for tetrahedral geometry[30] is 112.6°. Hence, the CN is bent

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(30) L. J. Guggenberger and R. Cramer, *J. Amer. Chem. Soc.*, 94, 3779 (1972).

Table XIII. Least-Squares Planes for $(C_2H_3CN)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$[a]

(1) $0.6565X + 0.7139Y - 0.2438Z - 5.810 = 0$
Ni (0.00), P(1) (0.00), P(2) (0.00), C(1) (0.07), C(2) (0.08)
(2) $-0.4264X + 0.5088Y + 0.7479Z - 8.035 = 0$
C(11) (0.00), C(12) (0.01), C(13) (0.01), C(14) (0.01), C(15) (−0.04), C(16) (0.02), C(17) (−0.02)
(3) $0.7061X - 0.1882Y + 0.6827Z - 1.845 = 0$
C(21) (−0.01), C(22) (−0.02), C(23) (−0.03), C(24) (0.02), C(25) (0.02), C(26) (−0.01), C(27) (0.03)
(4) $0.1296X + 0.7508Y + 0.6477Z - 1.437 = 0$
C(31) (−0.01), C(32) (0.01), C(33) (−0.01), C(34) (−0.01), C(35) (0.02), C(36) (0.00), C(37) (0.01)
(5) $-0.5518X + 0.4202Y + 0.7204Z - 3.622 = 0$
C(41) (−0.01), C(42) (−0.03), C(43) (−0.01), C(44) (0.00), C(45) (0.02), C(46) (0.00), C(47) (0.03)
(6) $-0.2194X + 0.8463Y - 0.4854Z + 6.747 = 0$
C(51) (−0.01), C(52) (0.02), C(53) (0.00), C(54) (−0.02), C(55) (0.02), C(56) (−0.01), C(57) (−0.01)

[a] The planes are based on the cartesian coordinate system (*a*, *b*, *c**). Following each plane are the atoms in the plane and the deviations from the plane except in plane 1 which was defined only by the Ni and two P atoms.

Table XIV. Least-Squares Planes for $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$[a]

(1) $-0.0132X + 0.8108Y - 0.5852Z + 1.869 = 0$
Ni(0.00), P(1) (0.00), P(2) (0.00), C(1) (0.12), C(2) (−0.04)
(2) $0.6545X + 0.6121Y + 0.4438Z - 4.287 = 0$
C(11) (0.02), C(12) (0.01), C(13) (−0.01), C(14) (0.03), C(15) (−0.03), C(16) (0.00), C(17) (−0.02)
(3) $0.7876X - 0.5327Y - 0.3098Z + 4.069 = 0$
C(21) (0.03), C(22) (0.03), C(23) (0.01), C(24) (0.01), C(25) (−0.03), C(26) (−0.01), C(27) (−0.04)
(4) $0.3239X - 0.1846Y + 0.9279Z - 6.111 = 0$
C(31) (−0.05), C(32) (−0.01), C(33) (−0.04), C(34) (0.01), C(35) (0.03), C(36) (0.02), C(37) (0.04)
(5) $0.7403X - 0.6561Y - 0.1465Z + 4.643 = 0$
C(41) (0.01), C(42) (−0.01), C(43) (0.00), C(44) (0.01), C(45) (−0.01), C(46) (0.00), C(47) (0.00)
(6) $0.9328X + 0.2149Y - 0.2894Z + 5.694 = 0$
C(51) (−0.02), C(52) (0.02), C(53) (−0.03), C(54) (−0.01), C(55) (0.04), C(56) (−0.02), C(57) (0.02)
(7) $0.4338X + 0.8700Y + 0.2341Z - 1.558 = 0$
C(61) (−0.01), C(62) (0.01), C(63) (−0.03), C(64) (0.02), C(65) (0.01), C(66) (−0.01), C(67) (0.01)

[a] The footnote to Table XIII applies here.

back about halfway to what might be expected for tetrahedral geometry. This dihedral angle is the same as that found in the acrylonitrile complex of iron,[31] $(C_2H_3CN)Fe(CO)_4$, but less than that found in tetrasubstituted complexes. The average value for the tetrafluoro-substituted olefin in $(C_5H_5)Rh(C_2F_4)(C_2H_4)$ is 114.3°.[30] The average value for C_2H_4 in the latter complex is 102.8°. The indication is that a single CN olefin substituent is bent back only slightly more than hydrogen in unsubstituted olefins. Substituents in tetrasubstituted complexes are bent back further as discussed previously.[30]

Perhaps the most interesting and novel aspect of the CN substituent effect on the Ni-olefin geometry is the displacement of the olefin along the C(1)-C(2) bond. The dotted line in Figure 2B points in the direction of an orbital symmetric with respect to the PNiP framework (bisecting the P-Ni-P angle). I believe this is an electronic effect wherein the olefin shifts to maximize the metal-olefin bonding, the driving force being the stabilization of the olefinic π^* orbital by the CN group. This effect was not mentioned in the paper[31] on $(C_2H_3CN)Fe(CO)_4$, the only other acrylonitrile structure determined. To test this hypothesis, the equatorial plane of the $(C_2H_3CN)Fe(CO)_4$ structure was drawn; this is shown in Figure 5. Clearly the metal-olefin geometry is the same as that found here, although the Fe-C(olefin) distances do not differ significantly. There is at least one example in the literature[32] of a Pt(II) complex where the Pt atom is markedly asymmetrically bonded to a complex diolefin; this has been rationalized in terms of a substituent CH_3 group destabilizing the metal-olefin bonding, leading to preferentially weaker bonds to one of the olefin carbon atoms.

The electronic effect of the CN substituent on the metal-olefin geometry is consistent with the σ-π formalism[33,34] for metal-olefin bonding. In this interpretation the CN lowers the olefin π^* orbital energy promoting d_π-π^* donation from the nickel atom. Increased population of the π^* olefin orbital decreases the C=C bond order. The shortening of the Ni–C bond by about 0.10 Å in the acrylonitrile complex relative to the nickel-ethylene complexes can be attributed to this effect. We might expect to see some concomitant increase in the C=C bond length in the acrylonitrile complex; however, the C=C bond lengths are equal. In all refinements except the last one the C–C bond length in the acrylonitrile complex was slightly longer, but equivalent in view of the errors involved.

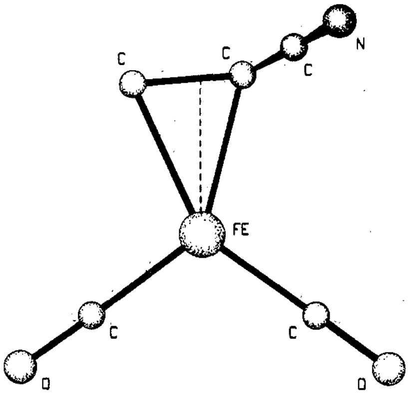

Figure 5. The equatorial plane of $(C_2H_3CN)Fe(CO)_4$ (coordinates from ref 31). The dotted line bisects the P–Ni–P angle.

The increased Ni-olefin bonding in the acrylonitrile complex parallels its increased stability. The equilibrium constant for nickel-olefin complex formation for the acrylonitrile complex is about 100 times greater than those for both the triphenylphosphine- and (tri-*o*-tolyl phosphite)nickel-ethylene complexes.[35]

The C=C distances in the (tri-*o*-tolyl phosphite)nickel complexes are the largest observed for unsubstituted metal-ethylene complexes (Table XII). This suggests that Ni(0) may be the most basic metal for donation to olefin π^* orbitals, but more data are needed to confirm this. Supporting evidence, however, is an unusually high chemical shift (τ 8.06) in the nmr spectrum and a low C=C stretching frequency (1487 cm^{-1}) for $(C_2H_4)Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$.[3,4]

The shortening of the Ni-P bond in the *o*-tolyl phosphite-ethylene complex compared to the triphenylphosphine complex is significant (0.06 Å). The indication is that tri-*o*-tolyl phosphite is a better π acceptor than triphenylphosphine. The same ordering was obtained from measuring CO stretching frequencies of $Ni(CO)_3L$ complexes.[5]

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[31] A. R. Luxmoore and M. R. Truter, *Acta Crystallogr.*, **15**, 1117 (1962).

[32] Table XII, ref *n*.

[33] M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).

[34] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[35] C. A. Tolman, to be submitted for publication.

Another structural comparison is with the recent structure[13] of bis(ethylene)(tricyclohexylphosphine)nickel. The pertinent data for that structure are 1.401 (14) Å for C=C, 2.014 (11) Å for Ni–C, and 2.196 (2) Å for Ni–P. These data are very similar to the data for $(C_2H_4)Ni[(C_6H_5)_3P]_2$ and minor differences can be attributed to the fact that this structure has one phosphine and two olefin ligands. The longer Ni–P distance in the tricyclohexylphosphine structure (2.196 (2) *vs.* 2.152 (5) Å) is consistent with the reasonable possibility for reduced π-acceptor properties of the phosphine ligand.

All Ni(0)- and Pt(0)-olefin complexes (Table XII) have the olefin ligand approximately in the PNiP plane (dihedral angle near 0°), whereas all comparable Pt(II) complexes have the olefin approximately perpendicular to this plane (dihedral angle near 90°). Mason[36] has suggested that the reason for this is that lowering the energy of the Pt p_z orbital in the 2+ oxidation state increases its involvement in bonding favoring a dihedral angle of 90°. Wheelock,[37] *et al.*, have been able to reproduce the position of the observed energy minimum with semiempirical molecular orbital calculations. The implication from their work seems to be that the small difference in energy between the two conformations is a net effect, difficult to pin down simply. In any case the 0 or 90° dihedral angle can hardly be a steric effect and the underlying reasons for the preferred conformation are still obscure.

Registry No. $(C_2H_3CN)Ni[o\text{-}CH_3C_6H_4O)_3P]_2$, 31666-48-5; $(C_2H_4)Ni[o\text{-}CH_3C_6H_4O)_3P]_2$, 31666-47-4.

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(36) R. Mason and G. B. Robertson, *J. Chem. Soc. A*, 492 (1969).

(37) K. S. Wheelock, J. A. Nelson, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 92, 5110 (1970).

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Crystal Structure and Single-Crystal Electron Paramagnetic Resonance Data for Bis[dihydrobis(1-pyrazolyl)borato]cobalt(II)

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The molecular and crystal structures of bis[dihydrobis(1-pyrazolyl)borato]cobalt(II), $[H_2B(pz)_2]_2Co$, have been determined from X-ray diffractometer data. Crystals are orthorhombic, in the polar space group $Pc2_1b$ (nonstandard setting of $Pca2_1$), with cell dimensions of $a = 11.200$ (12), $b = 14.268$ (15), and $c = 10.216$ (12) Å. The observed and calculated densities for four molecules per cell are 1.44 and 1.43 g/cm^3, respectively. The structure was solved by Patterson superposition and Fourier techniques and refined by least squares to a conventional R of 0.065. The crystal structure consists of the packing of discrete molecules which have two bidentate dihydro(1-pyrazolyl)borato ligands, $[H_2B(pz)_2]^-$, bonded to cobalt. The local cobalt atom coordination is a distorted tetrahedron with Co–N distances of 1.967 (12) Å, whereas the overall molecular symmetry is only approximately $C_2(2)$. Paramagnetic resonance data obtained on magnetically dilute systems at 4.2°K are presented for the parent complex and some substituted derivatives. In contrast to the corresponding bis[hydrotris(1-pyrazolyl)borato]cobalt(II) complexes, there are sizable changes in the apparent g values and hyperfine coupling constants with substitution. The resonance spectra are notable for the fact that it appears that only the $\pm{}^{3}/_{2}$ transition of the $^4A_2$ ground state is observed and, for this reason, they can only be partially analyzed.

Introduction

Numerous transition metal polypyrazolylborates of the types $M[R_2B(pz)_2]_2$ and $M[RB(pz)_3]_2$ have been synthesized.[1,2] The pyrazolylborato ligands $R_2B(pz)_2^-$ and $RB(pz)_3^-$ usually act as bidentate or tridentate chelating ligands, respectively, on coordination with transition metals. A variety of complexes are formed with the divalent transition metal ions having different metal atom configurations and coordination geometries yet maintaining fairly constant ligand characteristics. Optical, nmr, epr, Mossbauer, and magnetic susceptibility data have been reported for some of them.[3-9]

We report here the molecular and crystal structures of bis[dihydrobis(1-pyrazolyl)borato]cobalt(II), $[H_2B(pz)_2]_2Co$. This structure serves as a model for the tetrahedral transition metal-bis(1-pyrazolyl)borato complexes (Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}). The remaining bis(1-pyrazolyl)borato complexes have an essentially square-planar metal atom configuration.[4]

Comparisons are made with the structural data from the bidentate $H_2B[3,5\text{-}(CH_3)_2pz]_2Mo(CO)_2\text{-}\pi\text{-}C_3H_5$[10] and $H_2B[3,5\text{-}(CH_3)_2pz]_2Mo(CO)_2(C_7H_7)$[11] structures and the tridentate $[HB(pz)_3]_2Co$,[12] $HB(pz)_3Mo(CO)_2N_2C_6H_5$,[13] and $HB(pz)_3(COCH_3)Fe(CO)_2$[14] structures.

(1) S. Trofimenko, *J. Amer. Chem. Soc.*, 88, 1842 (1966).

(2) S. Trofimenko, *J. Amer. Chem. Soc.*, 89, 3170, 6288 (1967).

(3) J. P. Jesson, *J. Chem. Phys.*, 45, 1049 (1966).

(4) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Amer. Chem. Soc.*, 89, 3148, (1967).

(5) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Amer. Chem. Soc.*, 89, 3158 (1967).

(6) J. P. Jesson, *J. Chem. Phys.*, 47, 582 (1967).

(7) J. P. Jesson and J. F. Weiher, *J. Chem. Phys.*, 46, 1995 (1967).

(8) J. P. Jesson, J. F. Weiher, and S. Trofimenko, *J. Chem. Phys.*, 48, 2058 (1968).

(9) G. N. La Mar, J. P. Jesson, and P. Meakin, *J. Amer. Chem. Soc.*, 93, 1286 (1971).

(10) C. A. Kosky, P. Ganis, and G. Avitabile, *Acta Crystallogr., Sect. B*, 27, 1859 (1971).

(11) F. A. Cotton, M. Jeremic, and A. Shaver, *Inorg. Chim. Acta*, in press.

(12) M. R. Churchill, K. Gold, and C. E. Maw, Jr., *Inorg. Chem.*, 9, 1597 (1970).

(13) G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Crystallogr., Sect. B*, 27, 725 (1971).