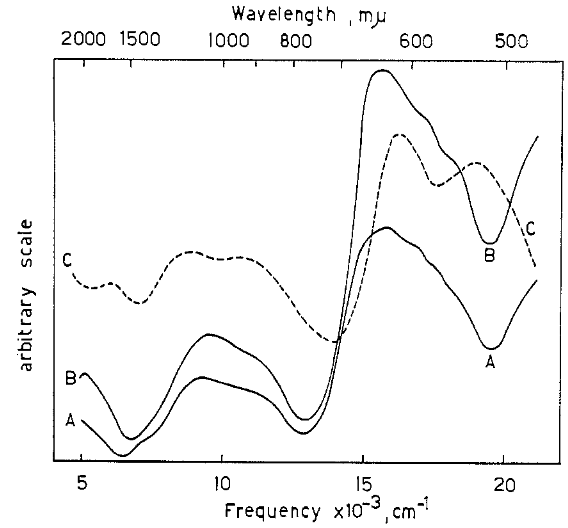

Figure 6.—Reflectance spectra of: $Co(MABen\text{-}NEt_2)Br_2$, curve A; $Co(MABen\text{-}NEt_2)Cl_2$, curve B; $Co(Me_5dien)Cl_2$, curve C.

sition is split into two components with an energy difference of *ca.* 1500 cm^{-1} is indicative of a high distortion in these complexes. The final band, which is due to a $^4A_2'(F) \rightarrow {}^4A_2'(P)$ transition, is expected to be almost independent of the ligand field strength and the geometry of the complex and is, as anticipated, around 16,000 cm^{-1}.

The magnetic moments are also in the same range as those found for other five-coordinate cobalt complexes (4.7–4.8 BM). All the physical measurements therefore suggest that a five-coordinate structure may also be assigned to the cobalt complexes, as is confirmed by the isomorphism between $Co(MABen\text{-}NEt_2)Br_2$ and the corresponding nickel complex.

Manganese Bromide.—The crystal field spectra of manganese complexes, as is well known, are of little use in determining the stereochemistry. The only useful correlation is therefore given by X-ray diffraction powder photograms which show the complex to be isomorphous with its cobalt and nickel analogs. This suggests that it may also be assigned a similar five-coordinate structure.

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The Crystal Structure of *trans*-Bis(phenylethynyl)bis(triethylphosphine)nickel(II), $[P(C_2H_5)_3]_2Ni(C{\equiv}CC_6H_5)_2$

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The crystal structure of *trans*-bis(phenylethynyl)bis(triethylphosphine)nickel(II), $[P(C_2H_5)_3]_2Ni(C{\equiv}CC_6H_5)_2$, has been determined from three-dimensional counter data at room temperature. The crystals are monoclinic ($P2_1/a$), with $a = 15.31$, $b = 10.88$, $c = 9.08$ A (all ±0.01 A), and $\beta = 105° 30' \pm 10'$. The structure consists of discrete molecules separated by ordinary van der Waals distances. Space group symmetry demands that the Ni atom and its four nearest neighbors be coplanar. The Ni–P bond length was found to be 2.220 ± 0.003 A, while the Ni–C distance is 1.879 ± 0.011 A. Both are significantly shorter than what is expected for "single" bonds and indicate substantial $d\pi\text{–}d\pi$ and $d\pi\text{–}p\pi$ interaction. The acetylenic and benzene C–C distances appear normal, as do the bond distances in the triethylphosphine groups. The benzene ring is tilted by $43.6 \pm 0.5°$ to the Ni–P–C plane.

Introduction

In general, transition metal to alkyl or aryl M–C σ bonds are unstable at room temperature as well as air and water sensitive. However, if strongly π-bonding ligands such as CO, π-C_5H_5, phosphines, or arsines are also present in the molecule, then stable alkyls and aryls can be prepared, *e.g.*, *cis*-$(PR_3)_2Pt(CH_3)_2$.[1] If, in addition to the presence of one of the π-bonding ligands in the molecule, the carbon σ bonded to the transition metal is involved in an acetylenic bond, then the metal–carbon bond is still further stabilized.[2] This increase in stability of the metal–carbon bond by the above ligands is generally attributed to the fact that these ligands tend to increase the separation between the highest filled and lowest empty MO's.[1–3] Similar reasoning can be used to explain the increasing M–C stability with increasing atomic number in the series Pt > Pd > Ni as observed by Chatt and Shaw. The transition metal–carbon σ bond can also be stabilized by making the carbon part of a highly fluorinated alkyl

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[1] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

[2] (a) G. E. Coates, "Organo-Metallic Compounds," Methuen and Co., Ltd., London, 1960, p 316; (b) G. E. Coates and F. Glockling in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York N. Y. 1960, Chapter 9.

[3] J. W. Richardson, ref 2b, Chapter 1.

system, and the structures of these compounds have been recently investigated by X-ray diffraction.[4,5] However, it is clear that the reasons for the increased stability of the M–C bond in the case of the fluoroalkyls are quite different than for the aryls and acetylides.[6]

The crystal structures of phenylethynyl(trimethylphosphine)copper(I) and -silver(I) have been determined by Corfield and Shearer,[7,8] but no crystal structures of any of the transition metal acetylides have been reported. Further, nickel acetylides seem to be formed as intermediates in the polymerization of terminal acetylenes by Ni(0) catalysts.[9] These facts prompted us to investigate the crystal structure of *trans*-bis(phenylethynyl)bis(triethylphosphine)nickel(II).

Crystals of *trans*-$[P(C_2H_5)_3]_2Ni(C{\equiv}CC_6H_5)_2$ were generously supplied to us by Dr. J. Chatt. Preliminary photographic data were collected on the Weissenberg and precession cameras. Cell constants were measured with calibrated precession photographs and then checked on the diffractometer; they agreed within the stated error. The crystals are monoclinic, $P2_1/a$, with $a = 15.31$, $b = 10.88$, $c = 9.08$ A (each ±0.01 A), and $\beta = 105° 30' \pm 10'$ (Cu Kα = 1.5418 A). There are two molecules in the unit cell and the X-ray density is 1.14 g cm^{-3}, in agreement with approximate density measurements that were limited by the rapid rate of solution of the compound in all organic solvents.

A single crystal 0.06 × 0.04 × 0.6 mm was mounted about the needle axis ([001] direction) on the GE single-crystal orienter and was used to collect 1120 independent *hkl* pieces of intensity data by a scan technique with a Picker diffractometer. The take-off angle was set at 4.0° and the receiving aperture was 6 × 8 mm high. Backgrounds were estimated by stationary count for 40 sec at ±1.67°, 2θ of the peak maxima. The peak was then scanned for 100 sec by the θ–2θ technique. The background was assumed to vary linearly across the peak and the integrated intensity was calculated as $I = I_{\text{scan}} - 1.25(B_1 + B_2)$, where B_1 and B_2 are the background counts at ±1.67°, 2θ, respectively, from the peak maximum. Only those reflections for which the integrated intensity was statistically above the background were retained. The intensity of a standard reflection was checked every 2 hr to ensure stability of operation.

The linear absorption coefficient (μ) for this compound with Cu Kα radiation is 25 cm^{-1}. No corrections were made for absorption. It has been recently shown[10] that absorption effects even with μ as large as 191 cm^{-1} do not significantly change the positional parameters; hence, we feel our positional parameters are probably within our esd. However, the estimate of error in our atomic thermal parameters may be somewhat optimistic.

The usual Lorentz-polarization corrections were made and the intensities reduced to squared structure factors.

Structure Determination and Refinement

With two molecules per cell in space group $P2_1/a$, the nickel atoms must be located on centers of symmetry. Therefore, the molecule must have the *trans* configuration, and Ni with its four nearest neighbor atoms must be coplanar. The Ni atoms were placed at 0, 0, 0 and $^1/_2$, $^1/_2$, 0 and the other atoms into the general set $\pm(x, y, z;\ ^1/_2 + x, ^1/_2 - y, z)$. We could have proceeded to solve the structure by Fourier analysis with signs determined by the Ni atoms, but we chose instead to compute a three-dimensional Patterson function.[11] From this Patterson function the phosphorus and acetylenic and benzene carbons atoms were located. The triethylphosphine carbon atoms were located from a three-dimensional electron density map calculated with phases based on the Ni, P, and acetylenic and benzene carbon atoms. Refinement was performed by full-matrix least squares[12] using anisotropic temperature factors with observations equally weighted and minimizing the function $\Sigma w(F_o - F_c)^2$. A refinement varying this same function with observations weighted on counting statistics and a 4% ignorance factor[13] gave essentially the same results. The scattering factors for neutral nickel, phosphorus, and carbon were obtained from a standard source.[14] Real anomalous dispersion[15] corrections of −3.2 and +0.31 electrons were made to the nickel and phosphorus scattering factors, but the small imaginary term was neglected. Final coordinate shifts were less than 3×10^{-4} of a cell edge and the final R,[16] weighted R, and standard error were 0.096, 0.103, and 1.50, respectively. Machine core storage limitations precluded the variation of all 142 variables simultaneously, and, consequently, we did the refinement in overlapping blocks of 125 variables. Although small peaks at reasonable locations were found for benzene hydrogen atoms in the final difference electron density map, the inclusion of these hydrogen atoms in the structure factor calculations did not significantly improve the agreement, and they were not included in the listing of the final calculated and observed structure factors of Table I. Otherwise the final three-dimensional electron density difference map was qualitatively featureless and showed no indication of triethylphosphine hydrogen atoms. Final atomic parameters and errors are listed in Table II.

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(4) M. R. Churchill, *Inorg. Chem.*, **4**, 1734 (1965).

(5) M. R. Churchill, *ibid.*, **6**, 185 (1967).

(6) F. A. Cotton and J. A. McCleverty, *J. Organometal. Chem.* (Amsterdam), **4**, 490 (1965).

(7) P. W. R. Corfield and H. M. M. Shearer, *Acta Cryst.*, **20**, 502 (1966).

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(9) L. S. Meriwether, M. F. Leto, E. C. Colthup, and W. G. Kennerly, *J. Org. Chem.*, **27**, 3930 (1962).

(10) R. C. Srivastava and E. C. Lingafelter, *Acta Cryst.*, **20**, 918 (1966).

(11) Patterson and electron density calculations were performed with a local modification of a program due to N. Baenziger for the IBM 7040.

(12) Least-squares calculations were made on the IBM 7040 with a local variation of the W. Busing, K. O. Martin, and H. Levy ORFLS program.

(13) S. W. Peterson and H. A. Levy, *Acta Cryst.*, **10**, 70 (1957).

(14) From the compilation of J. A. Ibers in "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202, 212.

(15) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

(16) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; weighted $R = \Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2$; standard error $= [\Sigma w(F_o - F_c)^2]/(NO - NV)^{1/2}$; where $NO = 1120$ and $NV = 125$ (actually there were 142 independent variables, but we could only vary 125 at any one time.)

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

• 0 K 0 •		
4	305	295
6	82	86
8	28	27
10	60	53
12	57	44
• 1 K 0 •		
2	137	131
3	447	440
4	227	197
5	97	65
6	81	76
8	48	35
12	24	5
• 2 K 0 •		
0	110	124
1	352	338
2	203	218
3	41	3
4	308	295
5	48	37
6	144	144
7	87	90
8	109	104
9	122	107
10	38	41
11	39	30
13	29	1
• 3 K 0 •		
1	242	243
3	198	179
4	149	128
5	326	292
6	90	91
7	179	157
9	127	114
8	101	98
10	67	58
11	50	35
12	26	28
• 4 K 0 •		
0	103	124
1	277	232
3	197	194
4	87	82
5	[illegible]	108
6	119	117
7	32	16
8	96	78
10	47	42
11	25	73
12	26	14
• 5 K 0 •		
1	75	74
2	19	34
3	130	158
4	22	38
5	135	133
7	155	147
9	63	80
11	40	25
• 6 K 0 •		
0	381	377
1	39	54
2	25	25
3	71	95
4	207	217
6	142	183
7	26	30
8	116	105
• 7 K 0 •		
1	100	90
3	78	79
4	69	81
5	128	130
7	138	142
8	52	41
9	40	38
10	45	40
• 8 K 0 •		
0	134	114
1	63	56
2	143	137
3	196	187
4	73	59
5	84	92
6	70	79
9	58	52
10	34	28
11	33	28
• 9 K 0 •		
1	215	193
2	124	124
3	138	131
4	97	76
8	30	31
9	27	18
10	38	28
11	25	27
• 10 K 0 •		
0	252	247
1	43	40
2	267	259
4	50	58
8	32	40
• 11 K 0 •		
1	177	156
2	77	84
3	47	62
4	37	44
5	29	22
• 12 K 0 •		
0	234	203
1	35	19
2	142	130
3	42	51
4	97	66
• 13 K 0 •		
1	102	89
3	110	88
• 14 K 0 •		
1	50	32
2	47	4
• 15 K 0 •		
2	44	39
• 0 K 1 •		
0	195	228
2	252	245
3	271	266
5	293	262
6	18	18
9	48	49
11	44	41
• 1 K 1 •		
2	326	269
3	263	229
4	171	148
5	100	92
6	86	72
7	57	43
9	94	96
10	46	27
11	52	46
• -1 K 1 •		
3	624	598
4	338	311
5	161	168
6	131	122
7	55	48
8	174	126
9	54	51
10	66	51
12	35	27
• 2 K 1 •		
1	40	39
3	355	322
4	288	270
5	71	69
6	116	115
9	37	21
10	50	44
12	56	49
• -2 K 1 •		
1	83	65
4	306	292
5	150	146
6	186	185
8	45	39
9	38	32
9	38	32
10	52	43
• 3 K 1 •		
1	416	393
2	39	19
3	185	191
4	281	254
6	62	61
7	35	28
9	54	50
• -3 K 1 •		
2	180	187
3	154	184
5	131	131
6	115	105
7	200	196
8	48	51
9	60	51
• 4 K 1 •		
0	617	603
1	77	82
2	185	191
3	41	24
4	248	212
5	102	105
6	126	121
7	35	32
8	100	92
9	47	51
10	42	33
10	42	33
• -4 K 1 •		
0	209	189
1	396	345
2	309	292
3	99	126
4	152	207
5	134	152
6	260	262
8	217	206
9	39	29
10	70	65
• 5 K 1 •		
1	189	163
2	269	266
3	204	219
4	232	241
5	210	211
6	13	22
6	13	22
7	118	111
8	52	55
9	67	52
• -5 K 1 •		
1	67	79
3	35	40
4	29	23
5	191	250
7	153	145
8	33	32
9	57	52
11	47	34
• 6 K 1 •		
0	80	104
1	173	141
2	129	133
3	48	38
4	188	216
5	114	115
6	168	172
8	113	111
10	47	43
• -6 K 1 •		
0	54	42
0	54	42
1	107	111
2	159	172
3	45	43
4	18	33
5	50	65
6	101	132
8	85	85
9	46	49
10	36	39
• 7 K 1 •		
1	120	103
2	152	137
3	61	55
4	29	24
5	205	206
7	126	121
9	62	63
• -7 K 1 •		
1	237	229
2	210	200
3	112	105
4	135	156
5	104	118
6	20	29
8	45	52
9	32	30
• 8 K 1 •		
0	47	44
1	24	0
2	148	145
3	102	108
4	139	135
5	67	76
6	128	136
8	124	122
9	47	37
10	40	33
• -8 K 1 •		
0	240	208
1	95	95
2	246	250
3	26	27
4	129	146
5	43	62
6	23	33
9	36	37
• 9 K 1 •		
1	113	99
2	29	24
3	121	119
4	112	106
5	116	109
6	24	42
7	72	69
8	40	32
• -9 K 1 •		
1	383	360
2	32	43
3	133	146
• 10 K 1 •		
0	150	165
1	33	29
2	108	96
3	47	52
5	32	29
• -10 K 1 •		
0	291	276
1	30	32
2	140	131
4	47	51
5	27	30
• 11 K 1 •		
1	215	210
2	86	83
3	122	117
4	66	61
6	43	43
• -11 K 1 •		
1	148	136
2	86	84
3	117	120
4	80	89
5	57	66
7	35	33
9	36	36
• 12 K 1 •		
0	49	39
2	94	83
4	39	27
5	34	29
• -12 K 1 •		
1	37	38
2	60	50
3	71	70
4	83	77
5	50	55
6	48	39
8	32	30
• 13 K 1 •		
1	76	58
2	25	19
• -13 K 1 •		
1	54	54
2	61	50
5	48	46
• 14 K 1 •		
0	90	81
2	76	63
3	62	56
5	42	38
• -14 K 1 •		
0	96	82
2	44	38
4	44	46
6	43	40
• 15 K 1 •		
2	63	52
3	30	26
4	56	49
• -15 K 1 •		
1	54	46
5	47	37
• -16 K 1 •		
3	38	33
• 0 K 2 •		
2	264	234
3	328	292
4	193	177
5	128	113
6	217	186
8	77	71
10	93	82
• 1 K 2 •		
1	157	171
2	46	19
3	270	236
4	30	25
5	154	117
6	73	58
8	58	63
9	33	27
11	44	34
• -1 K 2 •		
2	147	158
3	117	130
4	486	437
5	170	161
6	65	71
7	210	186
9	95	92
• 2 K 2 •		
0	309	333
2	212	207
4	59	60
5	95	85
6	30	14
7	65	51
• -2 K 2 •		
1	328	313
2	333	343
3	228	248
4	280	261
5	89	91
6	294	285
7	70	63
8	183	163
9	45	43
• 3 K 2 •		
1	151	174
3	294	292
4	41	29
5	114	98
• -3 K 2 •		
1	711	734
2	119	121
4	51	71
5	300	329
7	236	222
8	41	41
9	79	70
• 4 K 2 •		
0	757	749
1	120	116
2	317	288
3	184	194
4	45	48
5	62	58
6	32	38
7	39	38
• -4 K 2 •		
0	253	225
1	355	319
3	154	206
4	203	203
5	186	194
6	190	185
8	56	51
9	68	59
• 5 K 2 •		
1	394	390
2	98	87
3	159	140
4	188	208
5	105	115
9	45	51
• -5 K 2 •		
1	370	309
2	305	317
4	145	158
5	163	195
6	131	144
7	163	169
9	62	54
• 6 K 2 •		
0	44	48
1	92	86
2	96	99
3	214	221
4	192	195
5	60	58
6	94	110
8	91	92
9	31	34
• -6 K 2 •		
0	337	319
1	132	135
2	216	232
3	163	161
4	119	145
5	80	88
6	96	94
8	98	92
10	50	39
• 7 K 2 •		
1	120	130
2	80	68
3	188	184
4	82	90
5	221	236
6	81	93
7	163	178
9	69	74
• -7 K 2 •		
1	198	203
4	19	35
5	71	77
6	46	47
11	37	35
• 8 K 2 •		
0	89	92
1	43	41
4	146	158
6	129	130
8	54	54
• -8 K 2 •		
0	281	289
1	122	122
2	225	219
3	50	46
4	41	79
6	34	50
• 9 K 2 •		
1	98	103
2	85	93
3	85	94
4	50	58
5	66	73
6	55	65
7	49	52
• -9 K 2 •		
1	205	184
2	19	16
3	102	111
4	29	56
6	47	46
• 10 K 2 •		
1	31	36
2	123	128
3	160	158
4	111	116
5	70	70
6	68	74
8	56	61
• -10 K 2 •		
0	184	176
1	107	111
2	90	94
3	159	183
4	41	59
5	70	74
• 11 K 2 •		
4	71	74
5	34	42
• -11 K 2 •		
2	110	109
3	39	43
4	36	45
5	53	60
• 12 K 2 •		
0	64	66
1	32	26
3	26	34
• -12 K 2 •		
4	67	93
6	78	77
• 13 K 2 •		
1	85	87
3	70	66
• -13 K 2 •		
3	51	40
5	64	57
7	67	69
• 14 K 2 •		
0	95	85
2	66	61
• -14 K 2 •		
1	35	34
6	53	46
• -15 K 2 •		
1	57	43
3	44	43
• -16 K 2 •		
3	52	52
• 0 K 3 •		
0	52	28
1	155	138
2	252	210
4	94	88
6	150	152
8	113	111
9	60	59
10	45	42
11	38	35
• 1 K 3 •		
1	207	196
2	225	234
3	287	253
4	246	219
5	158	141
7	131	139
8	34	45
9	70	63
• -1 K 3 •		
1	78	49
2	13	19
3	282	250
5	317	311
7	250	241
9	96	78
• 2 K 3 •		
0	173	187
2	300	285
3	74	38
4	113	115
5	81	82
6	125	129
• -2 K 3 •		
0	137	154
1	79	100
2	61	54
3	40	56
4	185	177
5	67	74
6	289	304
7	54	55
8	172	169
9	37	36
10	67	66
• 3 K 3 •		
1	361	342
2	150	157
3	280	284
4	83	90
• 3 K 3 •		
5	27	34
8	41	39
11	44	39
• -3 K 3 •		
1	34	28
2	334	320
3	37	51
4	11	11
5	201	226
6	46	65
7	152	158
8	58	55
9	54	49
• 4 K 3 •		
0	224	219
1	164	149
2	228	236
3	36	46
4	79	76
5	61	65
• -4 K 3 •		
0	407	384
1	49	41
2	563	528
3	64	58
4	258	306
5	36	50
6	57	60
7	26	36
8	66	75
• 5 K 3 •		
1	320	322
2	133	133
3	198	193
4	49	48
• -5 K 3 •		
2	200	189
3	81	89
4	106	135
5	56	76
7	46	66
• 6 K 3 •		
0	372	356
1	138	141
2	186	183
3	202	212
4	160	170
5	94	106
6	94	96
9	47	44
• -6 K 3 •		
0	334	300
1	193	181
2	149	167
3	65	65
4	99	138
5	61	89
7	38	67
• 7 K 3 •		
1	89	89
2	84	83
3	86	71
4	184	195
5	67	62
• -7 K 3 •		
1	235	213
2	44	41
3	203	222
4	49	64
5	43	51
• 8 K 3 •		
0	90	77
2	116	126
4	107	101
6	70	87
8	82	83
• -8 K 3 •		
0	149	141
1	73	78
2	82	72
3	44	34
4	55	93
5	44	68
• 9 K 3 •		
3	42	38
5	143	145
7	90	94
• -9 K 3 •		
1	184	173
2	158	149
3	34	34
4	72	98
• 10 K 3 •		
2	48	57
4	44	49
6	61	67
• -10 K 3 •		
0	69	59
1	83	87
2	41	37
3	84	88
4	49	52
5	52	68
6	53	80
6	53	80
• 11 K 3 •		
2	49	40
3	67	68
• -11 K 3 •		
1	51	49
2	74	71
3	77	77
4	48	54
5	87	115
7	41	78
• 12 K 3 •		
0	47	54
2	48	46
3	50	46
• -12 K 3 •		
2	37	35
4	56	50
6	58	77
• 13 K 3 •		
1	62	58
3	33	31
• -13 K 3 •		
1	49	40
2	45	39
3	36	35
4	39	41
5	36	50
• 14 K 3 •		
0	71	73
• -14 K 3 •		
0	49	36
2	48	47
4	49	48
6	40	45
• -15 K 3 •		
3	43	39
• -16 K 3 •		
0	62	51
2	55	49
• 0 K 4 •		
0	27	39
1	49	42
2	32	46
4	262	241
5	51	38
6	254	235
8	115	107
• 1 K 4 •		
1	232	244
3	128	115
4	46	40
5	181	181
6	42	38
7	156	150
9	65	68
• -1 K 4 •		
2	185	165
5	209	193
6	79	84
7	125	124
9	60	66
• 2 K 4 •		
0	195	205
1	141	134
2	190	196
3	161	150
4	193	191
6	159	169
8	91	96
9	68	71
10	51	46
• -2 K 4 •		
1	208	197
2	52	76
3	244	225
4	130	148
5	136	142
6	69	68
8	87	88
• 3 K 4 •		
1	67	82
2	81	78
3	217	225
4	168	176
5	85	74
7	104	115
9	49	48
• -3 K 4 •		
1	171	162
2	121	115
3	116	120
4	210	211
5	136	146
8	32	47
9	29	42
10	55	60
• 4 K 4 •		
0	397	400
1	37	41
2	289	293
3	173	182
4	130	139
6	119	115
10	31	41
• -4 K 4 •		
0	227	199
1	156	127
3	124	125
4	61	66
9	44	50
• 5 K 4 •		
1	351	353
2	48	39
3	185	204
• -5 K 4 •		
1	366	312
2	102	92
3	190	225
4	100	116
5	31	38
• 6 K 4 •		
0	231	222
2	240	256
3	27	27
5	45	50
6	70	[illegible]
• -6 K 4 •		
0	469	434
1	269	238
2	313	348
3	133	131
4	82	108
5	63	90
• 7 K 4 •		
1	132	136
2	29	30
3	141	151
5	81	80
7	40	43
• -7 K 4 •		
1	239	238
2	71	78
3	92	112
5	59	93
• 8 K 4 •		
0	33	30
3	108	112
6	61	61
• -8 K 4 •		
0	237	215
1	5	3
2	183	199
3	36	41
4	86	124
6	35	109
• 9 K 4 •		
4	101	100
7	54	49
• -9 K 4 •		
1	68	79
2	83	88
3	80	88
4	40	54
5	43	67
7	97	108
• 10 K 4 •		
1	47	39
2	50	54
3	58	59
4	80	78
6	55	57
• -10 K 4 •		
0	47	44
1	64	66
3	49	61
4	68	77
6	100	109
• 11 K 4 •		
5	61	62
• -11 K 4 •		
2	54	48
3	51	51
5	57	81
7	36	75
• 12 K 4 •		
4	62	58
• -12 K 4 •		
1	59	59
3	66	72
4	37	45
• -13 K 4 •		
1	44	38
3	36	42
• -14 K 4 •		
0	54	42
2	47	50
• -15 K 4 •		
1	62	56
• -16 K 4 •		
0	60	52
• 0 K 5 •		
2	99	90
3	117	105
4	198	178
5	85	82
6	89	71
8	83	83
• 1 K 5 •		
1	47	46
2	71	77
3	125	115
4	28	4
5	172	166
7	121	128
9	52	58
• -1 K 5 •		
1	130	128
2	214	187
3	94	81
4	150	136
5	135	137
7	71	60
9	34	33
• 2 K 5 •		
1	71	68
3	28	33
4	125	120
6	187	179
8	92	99
• -2 K 5 •		
2	141	133
3	145	129
4	156	150
5	76	71
6	48	39
• 3 K 5 •		
1	136	129
2	62	53
3	138	137
4	17	34
5	225	224
7	103	101
9	47	51
• -3 K 5 •		
1	336	291
2	73	68
3	145	135
4	74	97
6	36	27
• 4 K 5 •		
0	104	120
1	80	81
2	151	146
3	113	109
4	70	63
5	62	63
• -4 K 5 •		
0	294	323
2	321	344
3	36	33
4	88	102
5	26	34
• 5 K 5 •		
1	195	193
2	136	141
3	119	125
4	204	209
• -5 K 5 •		
1	292	262
2	187	174
3	42	54
4	28	27
6	43	57
• 6 K 5 •		
0	211	223
2	120	120
3	63	61
4	69	85
5	39	32
6	63	64
• -6 K 5 •		
0	140	127
1	59	50
2	76	94
3	138	147
4	75	89
5	83	112
6	74	110
• 7 K 5 •		
1	95	94
3	61	61
4	64	71
• -7 K 5 •		
1	163	138
2	127	125
3	215	214
4	126	150
5	68	101
6	35	55
7	55	94
• 8 K 5 •		
0	91	97
2	128	139
3	39	41
4	46	48
• -8 K 5 •		
0	136	113
1	38	32
2	125	118
4	46	51
5	39	51
6	39	73
• 9 K 5 •		
1	116	123
2	57	58
3	55	68
4	45	44
• -9 K 5 •		
1	54	45
3	69	71
5	80	118
• 10 K 5 •		
0	40	39
3	54	58
• -10 K 5 •		
0	54	61
1	49	49
2	44	41
3	31	21
4	75	83
5	43	47
6	65	101
• 11 K 5 •		
2	42	39
• -11 K 5 •		
1	40	42
2	72	68
3	39	45
4	47	56
5	32	49
• -12 K 5 •		
0	67	59
1	28	34
2	40	35
3	46	52
5	40	53
• -13 K 5 •		
1	79	69
• -14 K [illegible] •		
0	68	[illegible]
2	42	41
• -15 K 5 •		
1	63	53
• 0 K 6 •		
1	91	70
2	144	147
3	121	116
4	108	102
6	69	68
8	54	52
• 1 K 6 •		
1	143	142
2	81	75
3	117	103
4	121	111
5	167	169
7	64	65
• -1 K 6 •		
1	274	259
3	199	192
4	72	73
5	64	66
• 2 K 6 •		
0	47	47
2	103	101
3	121	124
4	168	167
6	78	90
8	62	65
• -2 K 6 •		
2	284	273
3	74	80
4	83	84
• 3 K 6 •		
1	29	30
3	41	37
4	78	85
5	50	55
7	72	77
• -3 K 6 •		
1	294	258
3	160	149
• 4 K 6 •		
1	45	42
2	20	42
3	131	137
4	118	121
5	51	65
6	127	131
8	57	63
• -4 K 6 •		
0	177	227
1	48	37
2	179	169
3	91	83
5	67	58
• 5 K 6 •		
2	68	59
5	65	71
7	47	58
• -5 K 6 •		
1	165	127
2	87	80
3	87	93
4	101	104
• 6 K 6 •		
0	54	58
2	55	60
3	53	48
• -6 K 6 •		
0	65	75
1	48	40
2	60	52
3	61	86
4	71	67
6	74	88
7	54	11
• 7 K 6 •		
1	130	140
3	77	87
• -7 K 6 •		
1	92	81
5	77	90
• 8 K 6 •		
0	136	152
2	92	96
• -8 K 6 •		
1	49	47
3	51	53
4	85	88
6	80	108
• 9 K 6 •		
1	89	94
3	64	69
• -9 K 6 •		
1	32	30
3	77	83
• 10 K 6 •		
2	78	85
• -10 K 6 •		
0	60	62
2	49	47
3	73	68
4	58	68
5	39	50
• -11 K 6 •		
1	101	93
2	76	71
3	52	59
4	56	61
5	45	59
• -12 K 6 •		
0	100	100
2	61	64
• -13 K 6 •		
1	86	79
• -14 K 6 •		
0	86	80
2	48	41
• -15 K 6 •		
1	34	28
• 0 K 7 •		
2	229	227
3	94	88
4	104	98
• 1 K 7 •		
1	169	180
2	81	87
3	140	131
4	48	55
• -1 K 7 •		
1	205	211
3	62	64
• 2 K 7 •		
2	54	53
4	60	68
6	64	64
• -2 K 7 •		
2	178	169
4	52	53
• 3 K 7 •		
3	55	58
4	63	64
5	124	140
7	82	92
• -3 K 7 •		
1	188	163
2	71	66
3	113	108
4	64	61
• 4 K 7 •		
0	61	60
3	46	54
6	56	65
• -4 K 7 •		
2	77	75
3	89	78
5	53	41
6	42	45
• 5 K 7 •		
5	63	66
• -5 K 7 •		
1	50	35
2	92	76
4	55	60
5	82	85
7	61	64
• 6 K 7 •		
0	81	89
4	50	61
• -6 K 7 •		
3	36	39
4	78	73
6	80	86
• 7 K 7 •		
2	42	48
3	39	45
• -7 K 7 •		
2	51	41
3	71	68
5	61	79
7	47	64
• 8 K 7 •		
0	62	76
• -8 K 7 •		
3	57	56
5	53	50
• -9 K 7 •		
1	50	53
5	71	70
• -10 K 7 •		
0	106	106
2	80	74
4	32	58
• -11 K 7 •		
1	123	114
3	59	59
• -12 K 7 •		
0	134	124
2	83	76
• -13 K 7 •		
1	62	65
• 0 K 8 •		
2	99	95
3	73	67
• 1 K 8 •		
1	94	95
• -1 K 8 •		
1	140	135
3	117	103
• 2 K 8 •		
2	83	95
3	97	100
• -2 K 8 •		
2	94	76
3	62	65
4	73	65
• 3 K 8 •		
2	76	80
4	67	69
• -3 K 8 •		
1	56	49
2	49	45
4	61	63
5	67	75
• 4 K 8 •		
4	55	62
• -4 K 8 •		
2	58	52
3	84	75
4	77	83
6	67	76
• 5 K 8 •		
3	50	53
• -5 K 8 •		
3	64	67
5	83	78
• -6 K 8 •		
3	61	49
4	91	89
6	65	80
• -7 K 8 •		
1	50	42
2	47	45
4	66	62
5	62	65
• -8 K 8 •		
0	72	99
2	80	56
3	60	60
4	39	44
• -9 K 8 •		
1	79	66
3	58	46
• -10 K 8 •		
0	57	65
• -11 K 8 •		
1	68	55
• 1 K 9 •		
1	59	88
• -1 K 9 •		
2	91	83
4	77	72
• 2 K 9 •		
0	75	102
2	48	68
• -2 K 9 •		
2	56	46
3	72	66
• 3 K 9 •		
1	78	92
• -3 K 9 •		
1	49	33
3	88	76
• -4 K 9 •		
4	74	69
• -5 K 9 •		
3	54	43
• -6 K 9 •		
2	62	52
3	70	54
4	56	47
• -7 K 9 •		
1	67	62
2	62	54
3	50	44
4	55	56
• -8 K 9 •		
0	35	56
2	55	48
• -9 K 9 •		
1	65	61

[a] Columns 1, 2, and 3 are k, F_c, and F_o, respectively. $F_c = 10F(\text{calcd})$; $F(\text{calcd})_{\text{absolute}} = F(\text{calcd})/\text{scale factor}$; scale factor = 0.674 ± 0.001.

Interatomic distances, angles, and errors, as well as atomic thermal parameters,[17] are tabulated in Tables III and IV.

Results and Discussion

The structure is most readily described as molecular units, indicated by the perspective drawing of Figure 1, separated by ordinary van der Waals distances, Table III. Symmetry demands that within the molecule the Ni and its near-neighbor phosphorus and carbon atoms all lie in the same plane. In fact, the C_2, C_3, and C_8 atoms also lie in this same plane. The P–Ni–C_1 angle is within experimental error of the idealized 90° for a "square-planar" complex. The benzene ring is planar well within experimental error. The equation of the weighted best least-squares plane through the benzene carbon atoms is $0.6429x + 0.3951y - 0.6562z - 0.1107 = 0$, in which x, y, and z refer to an internal orthogonal coordinate system. The deviations from this plane are -0.017, $+0.024$, $+0.002$, -0.009, $+0.022$, and -0.019 A for C_3–C_8, respectively.

The observed Ni–P distance of 2.220 ± 0.003 A is considerably shorter than the 2.49 A than one might expect from the sum of the single-bond covalent radii[18] and indicates a substantial amount of Ni–P $d\pi$–$d\pi$ bonding. This no doubt contributes to the thermal and aerobic stability of this compound and in particular to the stabilization of the Ni–C σ bond. Although Pt–P distances of 2.315 ± 0.004, 2.298 ± 0.018,[19] and

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(17) Distances, angles, errors, and thermal parameters were calculated with a local version of the W. Busing, K. O. Martin, and H. Levy ORFFE program on the IBM 7040.

(18) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

(19) G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966).

Table II

Atom Positional and Temperature Parameters and Errors; $\sigma' = \sigma \times 10^4$

	x/a	$\sigma'(x/a)$	y/b	$\sigma'(y/b)$	z/c	$\sigma'(z/c)$
Ni	0	...	0	...	0	...
P	0.0931	2	0.9265	3	0.8713	4
C_1	0.0992	8	0.0331	12	0.1680	12
C_2	0.1660	8	0.0535	11	0.2735	14
C_3	0.2490	7	0.0735	13	0.3964	12
C_4	0.2618	9	0.1869	14	0.4748	15
C_5	0.3171	8	0.9816	13	0.4316	14
C_6	0.3425	10	0.2020	15	0.5969	17
C_7	0.3987	9	−0.0008	16	0.5491	18
C_8	0.4083	10	0.1083	17	0.6320	17
C_9	0.0844	10	0.0145	18	0.6939	15
C_{10}	0.1060	13	0.1550	21	0.7296	24
C_{11}	0.0623	9	0.7713	14	0.7981	16
C_{12}	0.0648	13	0.6780	16	0.9260	22
C_{13}	0.2185	8	0.9202	15	0.9712	17
C_{14}	0.2845	10	0.8749	19	0.8793	22

Thermal Parameters and Standard Deviations

Anisotropic Temperature Factors of the Form

$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; $\sigma' = \sigma \times 10^4$

Atom	β_{11}	σ'	β_{22}	σ'	β_{33}	σ'	β_{12}	σ'	β_{13}	σ'	β_{23}	σ'
Ni	0.0064	1	0.0120	3	0.0109	4	−0.0005	2	0.0004	2	−0.0006	3
P	0.0067	2	0.0133	4	0.0139	5	−0.0000	2	0.0014	2	−0.0013	4
C_1	0.0064	7	0.0168	19	0.0117	18	−0.0006	9	0.0012	9	−0.0008	14
C_2	0.0068	7	0.0113	14	0.0195	22	0.0011	8	0.0006	11	−0.0012	14
C_3	0.0057	7	0.0151	16	0.0133	18	−0.0005	9	−0.0007	9	−0.0009	16
C_4	0.0079	8	0.0170	18	0.0148	22	−0.0017	10	−0.0001	10	−0.0045	16
C_5	0.0068	7	0.0139	16	0.0212	23	0.0013	10	−0.0015	11	0.0019	17
C_6	0.0092	10	0.0186	21	0.0212	27	−0.0012	13	0.0001	13	−0.0034	19
C_7	0.0078	9	0.0156	18	0.0302	31	−0.0005	12	−0.0011	13	0.0031	24
C_8	0.0088	10	0.0174	21	0.0216	26	−0.0025	13	−0.0011	13	0.0022	20
C_9	0.0117	11	0.0223	24	0.0177	23	−0.0007	15	0.0052	12	0.0025	22
C_{10}	0.0152	16	0.0227	28	0.0451	50	0.0019	18	0.0108	22	0.0097	33
C_{11}	0.0089	9	0.0173	20	0.0210	27	0.0000	11	0.0033	12	−0.0026	19
C_{12}	0.0180	17	0.0130	19	0.0362	43	0.0002	15	0.0019	20	0.0016	23
C_{13}	0.0059	8	0.0224	22	0.0285	29	0.0002	11	0.0030	12	−0.0049	22
C_{14}	0.0072	9	0.0303	31	0.0453	46	0.0009	14	0.0063	17	−0.0041	31

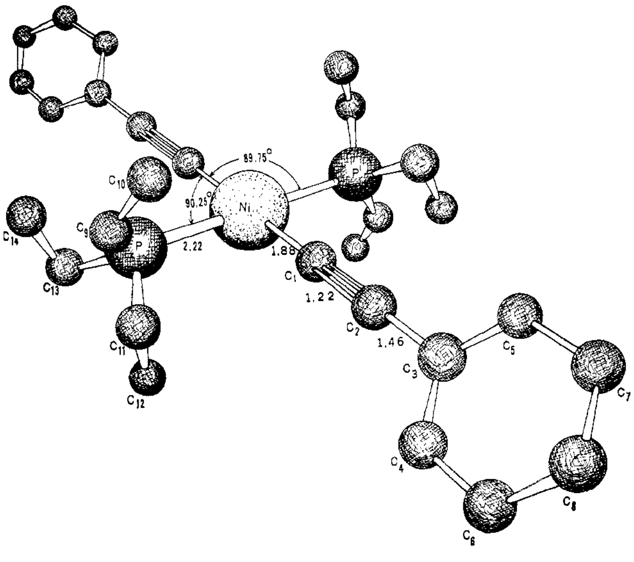

Figure 1.—Perspective view of *trans*-bis(phenylethynyl)bis(triethylphosphine)nickel(II) with the most important distances and angles indicated.

2.268 ± 0.008 A[20] have been observed in *trans* P–Pt–P configurations which indicate that the Pt–P bond contains considerable multiple bonding (2.41 A expected from covalent radii), it has been tacitly assumed in the past[2] that tertiary phosphines will form stronger dπ–dπ bonds with heavier transition metal (Pt > Pd > Ni) atoms without any supporting data. It is interesting to note that Ibers and Enemark found an Mn–P distance of 2.28 A in $Mn(NO)(CO)_2[P(C_6H_5)_3]_2$.[21] Our Ni–P distance indicates that, at least in this compound, the Ni–P dπ–dπ interaction seems to be as large as in the heavier transition metals of this group. Further, we believe that this is the first measurement of an Ni–P distance in a trialkylphosphine complex.

On the other hand, our Ni–C distance of 1.879 ± 0.011 A is significantly shorter than the 2.08 A expected from the sum of an sp carbon radius of 0.689 A (see below) and the Ni(II) radius of 1.39 A. This indicates a significant amount of dπ–pπ multiple bonding in the Ni–C bond. However, the carbon–carbon triple bond length in the acetylene moiety (C_1–C_2, 1.218 ± 0.014 A) is not significantly different from that in acetylene itself (1.204 ± 0.001 A).[22] Although the benzene C–C distances appear uniformly somewhat longer (Figure 1, Table III) than the 1.39 A expected for a benzene C–C

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[20] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

[21] J. A. Ibers, private communication. See also J. H. Enemark and J. A. Ibers, Abstracts, American Crystallographic Association Meeting, Atlanta, Ga., Jan 25–28, 1967, paper I8.

[22] B. D. Saksena, *J. Chem. Phys.*, **20**, 95 (1952).

TABLE III

INTERATOMIC DISTANCES (A), ANGLES (DEGREES), AND ERRORS[a]

Bonding Interatomic Distances and Angles

Ni–P	2.220 (3)	P–Ni–C_1	89.75 (36)
Ni–C_1	1.879 (11)	P–Ni–C_1	90.25 (36)
C_1–C_2	1.218 (14)	Ni–P–C_9	111.20 (52)
C_2–C_3	1.464 (15)	Ni–P–C_{11}	112.68 (46)
C_3–C_4	1.413 (17)	Ni–P–C_{13}	118.21 (47)
C_3–C_5	1.425 (16)	P–C_9–C_{10}	111.27 (1.12)
C_4–C_6	1.429 (17)	P–C_{11}–C_{12}	112.19 (1.02)
C_5–C_7	1.420 (16)	P–C_{13}–C_{14}	118.46 (1.10)
C_6–C_8	1.415 (20)	Ni–C_1–C_2	177.27 (1.10)
C_7–C_8	1.407 (21)	C_1–C_2–C_3	176.92 (1.33)
P–C_9	1.854 (14)	C_2–C_3–C_4	119.32 (1.16)
C_9–C_{10}	1.551 (24)	C_2–C_3–C_5	120.20 (1.16)
P–C_{11}	1.833 (15)	C_3–C_5–C_7	121.47 (1.32)
C_{11}–C_{12}	1.525 (21)	C_3–C_4–C_6	118.45 (1.29)
P–C_{13}	1.896 (12)	C_5–C_7–C_8	117.18 (1.39)
C_{13}–C_{14}	1.551 (20)	C_4–C_6–C_8	119.86 (1.37)
		C_6–C_8–C_7	122.46 (1.30)
		C_9–P–C_{11}	102.42 (73)
		C_9–P–C_{13}	105.26 (70)
		C_{11}–P–C_{13}	105.64 (67)

Nonbonding Intramolecular Distances

Ni–C_2	3.097 (12)	C_1–C_{13}'	3.132 (18)
Ni–C_3	4.558 (10)	C_2–C_9	3.993 (19)
P–C_1	2.902 (12)	C_2–C_{11}	3.882 (18)
P–C_1'	2.915 (12)	C_1–C_3	2.682 (15)
P–C_2	3.836 (12)	C_1–C_4	3.612 (17)
P–C_2'	3.784 (13)	C_1–C_5	3.594 (16)
P–C_{10}	2.816 (20)	C_2–C_{13}'	3.132 (18)
P–C_{12}	2.792 (18)	C_3–C_9	5.038 (19)
P–C_{14}	2.967 (15)	C_3–C_{11}	4.919 (18)
C_1–C_9	3.411 (18)	C_4–C_{11}	4.945 (19)
C_1–C_{11}	3.339 (18)	C_3–C_{13}'	4.115 (19)
C_1–C_{12}	3.959 (21)	C_5–C_{13}'	4.099 (19)

Nonbonding Intermolecular Distances

C_4–C_{14}	3.720 (24)	All others	>3.900

[a] Primes refer to atoms related by the center of symmetry of the Ni site. The dihedral angle between normals to planes defined by Ni–P–C_1 and the benzene ring is 43.6 ± 0.5°.

TABLE IV

RMS ATOMIC DISPLACEMENTS IN THE DIRECTION OF THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS (A)

$\sigma' = \sigma \times 10^3$

Atom	R_1	σ'	R_2	σ'	R_3	σ'
Ni	0.199	3	0.267	4	0.284	3
P	0.227	4	0.278	4	0.288	4
C_1	0.210	16	0.275	14	0.319	18
C_2	0.246	16	0.256	16	0.320	16
C_8	0.201	16	0.290	14	0.302	16
C_4	0.206	18	0.324	16	0.334	17
C_5	0.222	17	0.297	17	0.348	16
C_6	0.255	18	0.342	20	0.356	18
C_7	0.265	17	0.300	19	0.395	19
C_8	0.254	18	0.299	20	0.386	20
C_9	0.248	17	0.356	18	0.374	20
C_{10}	0.320	23	0.385	22	0.463	25
C_{11}	0.275	18	0.315	16	0.333	19
C_{12}	0.277	21	0.365	21	0.476	21
C_{13}	0.254	16	0.311	18	0.388	19
C_{14}	0.272	18	0.399	22	0.448	23

distance, our errors are, unfortunately, sufficiently large that these differences are not statistically significant. The C_2–C_3 distance of 1.46 A might appear at first glance to be somewhat short for a carbon–carbon single bond, but it must be borne in mind that this is a C–C bond involving an sp- and an sp^2-hybridized carbon atom. If the sp carbon radius is taken as half the carbon–carbon single-bond distance in diacetylene[23] or the methyl carbon to acetylenic carbon distance in methylacetylene[24] minus 0.772 A, one finds a value of 0.689 A. The aromatic sp^2 carbon radius of 0.75 A can be taken from nitromesitylene,[25] biphenyl,[26] or toluene.[27] Hence, one would predict a C_2–C_3 distance of 1.44 A and the observed distance is not significantly different at 1.464 ± 0.015 A. Therefore, we conclude that if there is any substantial conjugative effect due to nickel–carbon bonding, it is not discernible from our data. This lack of observed bond elongation due to a possibly conjugated chain is supported by the fact (Table III) that the benzene ring is tilted 43.6 ± 0.5° to the plane defined by the Ni, P, and C_1 atoms. This tilting of the benzene ring is most likely due to nonbonded intra- and intermolecular contacts.

The P–C carbon distance that is expected from the single-bond radii is 1.87 A. Our observed values are 1.854 ± 0.014, 1.833 ± 0.015, and 1.896 ± 0.012 A, none of which is significantly different from the expected value; however, the shortest seems to be significantly shorter than the longest for no obvious reason. Further, the carbon involved in the longest P–C distance also has a P–C–C angle significantly different from the idealized tetrahedral value at 118.46 ± 1.1°. Nevertheless, the trialkylphosphine C–C distances are well within statistical error of the expected 1.54 A.

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