THE STRUCTURE OF BIS(tert-BUTYL ISOCYANIDE)(DIPHENYL-ACETYLENE)NICKEL(0), $Ni(C_6H_5C{\equiv}CC_6H_5)[(CH_3)_3C{-}N{\equiv}C]_2$

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(Received August 16th, 1971)

SUMMARY

The structure of the diphenylacetylene complex $Ni(C_6H_5C{\equiv}CC_6H_5)[(CH_3)_3C{-}N{\equiv}C]_2$ has been determined from X-ray data collected by counter methods. The compound crystallizes in space group $C_{2h}^5{-}P2_1/a$ with eight molecules in the cell of dimensions $a = 29.580(12)$, $b = 10.803(5)$, $c = 15.136(5)$ Å, $\beta = 107.85(5)°$. The structures of the two independent molecules in the asymmetric unit are similar in overall detail. In each, the Ni atom has trigonal coordination if the diphenylacetylene is regarded as a monodentate ligand, and the inner coordination sphere is essentially planar. The diphenylacetylene carbon atoms are equidistant from the metal atom in each of the two independent molecules. The average C–C distance of 1.285(20) Å is intermediate between normal C=C and C≡C bond lengths. The phenyl rings of the coordinated diphenylacetylene are bent away from the metal by about 31° from the C≡C bond axis.

INTRODUCTION

There has been considerable recent interest in the chemistry of small molecules linked to transition metals. Many simple ligands show enhanced reactivity when they are coordinated to a transition metal and an understanding of this effect has been greatly assisted by structural studies. Coordinated olefins and acetylenes are among the ligands that exhibit enhanced chemical reactivities. While some precise structural data[1] are available on olefin complexes, there is a scarcity of similar data on complexes in which a discrete RC≡CR molecule is linked to a single transition metal. Indeed, *trans*-dichloro(π-di-tert-butylacetylene)-*p*-toluidineplatinum(II) is the only such compound for which precise structural data have been reported[2]. A preliminary account[3] of the structure of bis(triphenylphosphine)(diphenylacetylene)platinum(0) has been published and rather inprecise structural data are available on two niobium–diphenylacetylene complexes[4,5]. Other known acetylene–transition metal structures[6-11] involve the RC≡CR molecule in a bridging position between two or more metal atoms.

Within the last few years, the chemistry of some π-complexes of nickel(0) has attracted attention. In this paper we report the structure of the complex bis(tert-butyl isocyanide)(diphenylacetylene)nickel(0), $Ni(C_6H_5C{\equiv}CC_6H_5)[(CH_3)_3C{-}N{\equiv}C]_2$.

This determination was undertaken to provide additional data on the bonding of acetylenes to transition metals, and we were also interested in comparing the structure with those of the closely related complexes bis(tert-butyl isocyanide)(tetracyanoethylene)nickel(0)[12], $Ni[(CN)_2C=C(CN)_2][(CH_3)_3C-N\equiv C]_2$, and bis(tert-butyl isocyanide)(azobenzene)nickel(0)[13], which have recently been completed in this laboratory.

EXPERIMENTAL

Preparation

The crystals of $Ni(C_6H_5C\equiv CC_6H_5)[(CH_3)_3C-N\equiv C]_2$ used in this study were prepared by the method of Otsuka and co-workers[14] and were crystallized from diethyl ether as very air-sensitive, yellow plates. Crystals obtained from hexane were more needle-like in habit but gave identical precession photographs.

Crystal data

$NiC_{24}H_{28}N_2$; mol. wt. 402.7; monoclinic, $a=29.580(12)$, $b=10.803(5)$, $c=15.136(5)$ Å, $\beta=107.85(5)°$; [Temp. 24°, $\lambda(Cu-K_{\alpha 1})$ 1.54056 Å]; $U=4604$ Å³, $d_c=1.17$ g/cm³ for $Z=8$ (the extreme air sensitivity of the compound precluded an experimental density determination). Linear absorption coefficient for $Cu-K_\alpha$ radiation, μ 13 cm^{-1}.

Precession photographs taken with $Cu-K_\alpha$ radiation (λ 1.5418 Å) of zero and first level zones showed systematic absences of $0k0$ reflections when $k\neq 2n$ and $h0l$ reflections when $h\neq 2n$. These absences are characteristic of the monoclinic space group C_{2h}^5–$P2_1/a$.

Intensity measurements were made with a Picker Four Circle Diffractometer (FACS-1) using $Cu-K_\alpha$ radiation prefiltered by 0.5 mm Ni foil. The procedure used for collection of the diffractometer data has been described elsewhere[15,16]. A crystal of approximate dimensions $0.040 \times 0.064 \times 0.098$ cm was mounted in a pre-dried, nitrogen filled glass capillary and sealed with the longest crystal edge roughly parallel to the capillary walls.

The half-widths of a number of narrow-source, open-counter ω-scans ranged from 0.06 to 0.21°, indicating that the mosaicity of the crystal was acceptably low. The setting angles of 12 reflections were determined manually through a narrow vertical slit at 1.5° takeoff angle. From these observations the crystal orientation and preliminary values of the cell parameters were derived by a least-squares procedure[15,16].

For data collection, $Cu-K_\alpha$ radiation was used, the intensities being measured by the θ–2θ technique at a takeoff angle of 3.0°. The counter was positioned 31 cm from the crystal and was preceded by an aperture of dimensions 7×7 mm. The pulse height analyzer was set to admit 90% of the $Cu-K_\alpha$ peak. Copper foil attenuators were automatically inserted if the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan.

The data were collected in five shells; $2\theta \leqslant 55.0°$, $55.0 < 2\theta \leqslant 66.0$, $66.0 < 2\theta \leqslant 82.0, 82.0 < 2\theta \leqslant 84.5$. Data collection was terminated because the last shell yielded relatively few intensities above background. Reflections were scanned at 1° in 2θ per minute out to 2θ 74° and thereafter at 0.5° per minute. A symmetric scan range of $\pm 0.9°$ in 2θ from the calculated scattering angle was employed for all reflections. Background counts of 10 sec were taken at each end of the scan out to 2θ 66°; these were

increased to 20 sec between $66°$ and $82°$, and subsequently to 40 sec for the final shell.

The intensities of three standard reflections were measured periodically (every 75 reflections). The standard deviations of these reflections were computed on the basis of the agreement among the 52 observations made for each standard during the seven days of data collection. These standard deviations were two to four times the expected values but there was no trend in the variations.

All data were processed as previously described[15,16]. A value of 0.03 was used for p in the estimation of $\sigma(F_0^2)$. Of the 3064 independent reflections observed, 2493 obeyed the condition $F_0^2 > 3\sigma(F_0^2)$, and only these reflections were used in subsequent calculations. To correct for the absorption of the crystal, the dimensions of the crystal were determined by means of a micrometer eyepiece; the calculated transmission factors ranged from 0.42 to 0.64*.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using conventional Patterson, least-squares, and Fourier methods. From a Patterson synthesis on the complete data set, it was possible to locate the nickel atom position for each of the two independent molecules in the asymmetric unit. These metal atom positions were confirmed by a direct methods approach. Several cycles of refinement, each followed by a difference Fourier synthesis led to positions for all other non-hydrogen atoms. The agreement factors $R(\Sigma\Delta/\Sigma|F_0|)$, $\Delta = ||F_0| - |F_c||)$ and $R_w[(\Sigma w \cdot \Delta^2/\Sigma w \cdot F_0^2)^{\frac{1}{2}}]$ were 0.204 and 0.261 respectively.

Refinement of the structure was continued by the method of full-matrix least-squares, the function minimized being $\Sigma w \cdot \Delta^2$, where $w = 4F_0^2/\sigma^2(F_0^2)$. At this stage of the refinement the phenyl rings were constrained to D_{6h} symmetry[17], and the C–C bond distance was fixed at 1.39 Å. The atomic scattering factors for Ni, C, and N used in all calculations were from the tabulation in International Tables for X-ray Crystallography[18]; the values for hydrogen were those of Stewart et al.[19] The anomalous dispersion corrections of Cromer[20] for Ni were applied to the calculated structure factors[21].

After correction for absorption, a cycle of refinement in which all nongroup atoms were assigned isotropic thermal parameters, and each of the phenyl rings an overall group thermal parameter, led to R and R_w values of 0.161 and 0.213, respectively. Several interrelated cycles of blocked-matrix least-squares refinements**, in

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* In addition to various local programs for the CDC 6400, computer programs used in this work include local versions of Dewar's FAME program, Zalkin's FORDAP Fourier program, Main, Woolfson, and Germain's direct methods programs, Coppens, Leiserowitz and Rabinovich's absorption program, Busing and Levy's ORFFE function and error program, Johnson's ORTEP thermal ellipsoid plotting program, and Watkin's RBANG group orientation program. Our least-squares program NUCLS, in its nongroup form, closely resembles the Busing-Levy ORFLS program.

** The method used here involved calculation of a structure factor for the two diphenylacetylene units plus the C≡N part of each tertiary butyl isocyanide group, and the subsequent addition of these contributions plus the contributions from all hydrogen atoms into a least-squares refinement of the parameters for the two nickel atoms and the (C_3C) section of each tert-butyl isocyanide group. Subsequently, the contribution from a structure factor calculation for $(C_3C)_4$ was added into the refinement of the parameters for the $Ni(C_6H_5C≡CC_6H_5)(C≡N)_2$ section of each molecule. In later refinements, a different blocking procedure was used. Here, each complete molecule, along with the second nickel atom and the scale factor were refined in full-matrix fashion.

TABLE 1

POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS[a] FOR INDIVIDUAL ATOMS, Ni(C$_6$H$_5$C≡CC$_6$H$_5$)[(CH$_3$)$_3$C–N≡C]$_2$

Atom	x	y	z	β_{11}[ab]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule 1									
Ni	0.26301(6)	0.13661(15)	0.24087(10)	18.0(3)	105.3(20)	44.1(10)	−2.7(7)	7.7(4)	7.1(12)
N(1)	0.2625(3)	0.3071(9)	0.0864(7)	23(2)	105(11)	69(7)	1(4)	16(3)	7(8)
N(2)	0.3592(4)	0.1214(9)	0.3760(7)	20(2)	156(13)	61(7)	9(5)	5(3)	15(8)
C(1)	0.2008(4)	0.0764(9)	0.2199(7)	17(2)	89(12)	60(7)	1(4)	15(3)	− 24(8)
C(2)	0.2287(4)	0.0265(9)	0.2927(7)	18(2)	82(12)	42(6)	5(4)	5(3)	19(7)
C(3)	0.2638(4)	0.2417(11)	0.1484(8)	19(2)	117(15)	58(8)	9(5)	11(3)	7(9)
C(4)	0.3226(5)	0.1312(11)	0.3210(8)	23(3)	133(14)	46(8)	4(6)	7(4)	23(9)
C(5)	0.2599(5)	0.3860(11)	0.0058(8)	33(3)	96(14)	60(8)	12(5)	22(4)	35(10)
C(6)	0.4045(5)	0.1083(15)	0.4518(9)	24(3)	215(23)	72(9)	− 11(7)	− 5(5)	− 15(13)
C(7)	0.2114(6)	0.3979(21)	−0.0519(13)	24(3)	577(50)	162(17)	− 1(10)	− 5(6)	204(25)
C(8)	0.2814(9)	0.5040(19)	0.0418(12)	112(9)	269(29)	92(12)	−102(14)	− 1(8)	53(16)
C(9)	0.2869(8)	0.3281(16)	−0.0464(13)	81(7)	247(26)	163(16)	57(11)	84(10)	103(17)
C(10)	0.4194(8)	0.2288(20)	0.4870(13)	73(7)	301(34)	140(16)	− 19(12)	−45(8)	5(20)
C(11)	0.3978(7)	0.0235(18)	0.5241(13)	56(5)	362(34)	131(15)	− 44(11)	−25(7)	149(21)
C(12)	0.4411(7)	0.0619(37)	0.4113(16)	35(5)	1254(120)	171(21)	77(19)	−23(8)	−253(43)
Molecule 2									
Ni	0.48442(8)	0.25397(19)	−0.24653(13)	26.6(4)	148.5(26)	68.0(13)	−0.2(8)	7.6(6)	−8.7(14)
N(1)	0.3993(5)	0.1250(13)	−0.2272(9)	28(3)	208(19)	115(9)	9(6)	28(5)	− 20(11)
N(2)	0.4511(4)	0.4987(13)	−0.3348(8)	30(2)	140(17)	92(9)	5(5)	6(4)	10(10)
C(1)	0.5375(5)	0.1462(13)	−0.2044(8)	27(3)	140(77)	72(9)	1(6)	11(4)	9(10)
C(2)	0.5508(5)	0.2461(13)	−0.2361(8)	25(3)	174(19)	57(8)	2(6)	4(4)	15(10)
C(3)	0.4311(5)	0.1754(14)	−0.2323(10)	24(3)	193(22)	80(9)	0(6)	13(5)	8(11)
C(4)	0.4629(5)	0.4060(13)	−0.2989(8)	25(3)	152(20)	75(10)	7(6)	4(4)	27(12)
C(5)	0.3612(8)	0.0617(22)	−0.2141(15)	41(5)	253(33)	148(17)	11(11)	35(8)	40(19)
C(6)	0.4424(6)	0.6197(16)	−0.3752(13)	37.(4)	181(25)	125(14)	8(8)	13(6)	41(18)
C(7)	0.3596(9)	−0.0596(28)	−0.2498(20)	59(7)	412(47)	303(33)	41(16)	78(13)	40(35)
C(8)	0.3211(9)	0.1234(31)	−0.2501(31)	38(6)	553(67)	750(85)	2(16)	82(18)	346(60)
C(9)	0.3702(10)	0.0276(35)	−0.1150(17)	88(10)	927(95)	168(22)	−122(26)	68(12)	− 8(39)
C(10)	0.4697(12)	0.7064(17)	−0.3032(18)	142(13)	129(33)	250(25)	− 13(14)	−41(15)	62(21)
C(11)	0.4529(12)	0.6200(20)	−0.4583(17)	132(13)	239(32)	172(20)	42(16)	41(14)	118(24)
C(12)	0.3911(7)	0.6491(25)	−0.4010(29)	29(4)	470(50)	741(67)	43(13)	39(14)	396(50)

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the less significant digits. [b] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}\cdot h^2 - \beta_{22}\cdot k^2 - \beta_{33}\cdot l^2 - 2\beta_{12}\cdot h\cdot k - 2\beta_{13}\cdot h\cdot l - 2\beta_{23}\cdot l\cdot k)$.

which all non-phenyl atoms were allowed to vibrate anisotropically, reduced R and R_w to 0.105 and 0.147, respectively. A difference Fourier map then revealed peaks which could be ascribed to most of the hydrogen atoms of the phenyl rings and methyl groups, despite the very high thermal motions exhibited by these carbon atoms. These hydrogen atom positions were idealized, and fixed contributions for all hydrogen atoms were included in all further structure factor calculations; the C–H distance was taken as 1.0 Å, and the temperature factor of each hydrogen atom was set equal to that of the carbon atom to which it was attached. Several further cycles of refinement reduced R and R_w to 0.096 and 0.124, respectively. In two final cycles, the phenyl carbon atoms were freed from their group constraints, and the refinement converged to R 0.091 and R_w 0.111.

In the final cycle no parameter shifted by more than 0.4 of its estimated standard deviation. The standard deviation of an observation of unit weight is 5.36.

An examination of $|F_o| vs. |F_o|$ as a function of Miller indices, the value of $|F_o|$ and scattering angle indicates that agreement is relatively worse at the lower scattering angles. A similar trend was noted in the analogous azobenzene structure[13], where the carbon atoms of the tert-butyl groups also exhibited considerable thermal motion.

TABLE 2

POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR PHENYL CARBON ATOMS

Atom	x	y	z	B (Å^2)
Molecule 1				
C(13)	0.1529(4)	0.0832(9)	0.1521(7)	4.9(2)
C(14)	0.1192(5)	−0.0057(12)	0.1558(9)	7.7(3)
C(15)	0.0744(5)	−0.0034(14)	0.0902(11)	9.9(4)
C(16)	0.0652(5)	0.0809(14)	0.0209(10)	9.2(4)
C(17)	0.0963(5)	0.1675(12)	0.0147(9)	7.8(3)
C(18)	0.1418(4)	0.1681(10)	0.0811(8)	6.4(3)
C(19)	0.2336 4)	−0.0511(10)	0.3691(7)	5.0(2)
C(20)	0.1992(6)	−0.0639(17)	0.4092(13)	12.8(5)
C(21)	0.2035(8)	−0.1505(21)	0.4868(16)	15.7(7)
C(22)	0.2451(7)	−0.1989(16)	0.5217(12)	11.7(5)
C(23)	0.2788(8)	−0.2028(20)	0.4851(16)	15.4(7)
C(24)	0.2738(6)	−0.1161(16)	0.4081(12)	11.5(5)
Molecule 2				
C(13)	0.5506(5)	0.0245(13)	−0.1645(9)	7.5(3)
C(14)	0.5914(5)	−0.0331(13)	−0.1653(9)	8.5(3)
C(15)	0.6023(5)	−0.1538(14)	−0.1318(10)	10.1(4)
C(16)	0.5729(6)	−0.2139(15)	−0.0925(11)	11.0(4)
C(17)	0.5320(7)	−0.1605(17)	−0.0868(12)	12.8(5)
C(18)	0.5203(6)	−0.0365(15)	−0.1249(11)	11.1(4)
C(19)	0.5873(5)	0.3232(12)	−0.2544(8)	7.0(3)
C(20)	0.6251(5)	0.2734(13)	−0.2716(10)	9.2(4)
C(21)	0.6607(6)	0.3507(16)	−0.2909(11)	10.6(4)
C(22)	0.6533(6)	0.4721(16)	−0.2924(11)	10.9(4)
C(23)	0.6181(6)	0.5268(15)	−0.2718(11)	10.9(4)
C(24)	0.5829(5)	0.4509(14)	−0.2489(9)	9.0(4)

We ascribe the poor agreement at low scattering angles and the relatively high value of R to improper handling within the model of the vibrations of these carbon atoms together with those of the phenyl carbon atoms. Experience in this laboratory with similar data collection procedures on similar types of crystals does not lead us to believe that the data are at fault. As evidence of this a comparison was made of the $|F_o|$ values for the 87 pairs $0kl$ and $0k\bar{l}$ reflections. The average agreement was 1.9%. No extinction corrections were deemed necessary.

TABLE 3

IDEALIZED POSITIONAL COORDINATES FOR HYDROGEN ATOMS[a]

Atom	x	y	z	Atom	x	y	z
Molecule 1				*Molecule 2*			
C(7) H(1)	0.188	0.337	−0.045	C(7) H(1)	0.393	−0.102	−0.235
C(7) H(2)	0.196	0.486	−0.029	C(7) H(2)	0.338	−0.126	−0.237
C(7) H(3)	0.206	0.420	−0.119	C(7) H(3)	0.349	−0.060	−0.326
C(8) H(1)	0.315	0.501	0.071	C(8) H(1)	0.311	0.132	−0.323
C(8) H(2)	0.273	0.570	−0.011	C(8) H(2)	0.291	0.100	−0.236
C(8) H(3)	0.265	0.539	0.089	C(8) H(3)	0.326	0.219	−0.230
C(9) H(1)	0.299	0.242	−0.023	C(9) H(1)	0.373	0.097	−0.081
C(9) H(2)	0.268	0.317	−0.116	C(9) H(2)	0.334	−0.014	−0.116
C(9) H(3)	0.317	0.378	−0.046	C(9) H(3)	0.390	−0.041	−0.100
C(10)H(1)	0.400	0.268	0.520	C(10)H(1)	0.502	0.661	−0.273
C(10)H(2)	0.454	0.228	0.532	C(10)H(2)	0.489	0.769	−0.352
C(10)H(3)	0.421	0.287	0.434	C(10)H(3)	0.458	0.756	−0.278
C(11)H(1)	0.365	0.021	0.525	C(11)H(1)	0.454	0.531	−0.490
C(11)H(2)	0.407	−0.067	0.512	C(11)H(2)	0.439	0.676	−0.512
C(11)H(3)	0.420	0.044	0.589	C(11)H(3)	0.493	0.640	−0.447
C(12)H(1)	0.455	0.122	0.376	C(12)H(1)	0.372	0.600	−0.380
C(12)H(2)	0.471	0.018	0.459	C(12)H(2)	0.382	0.735	−0.420
C(12)H(3)	0.428	−0.012	0.363	C(12)H(3)	0.377	0.612	−0.485
C(14)H	0.127	−0.068	0.207	C(14)H	0.613	0.010	−0.197
C(15)H	0.051	−0.068	0.091	C(15)H	0.632	−0.195	−0.137
C(16)H	0.033	0.083	−0.030	C(16)H	0.581	−0.298	−0.066
C(17)H	0.091	0.235	−0.035	C(17)H	0.511	−0.197	−0.055
C(18)H	0.167	0.235	0.081	C(18)H	0.492	0.008	−0.114
C(20)H	0.167	−0.017	0.381	C(20)H	0.629	0.182	−0.276
C(21)H	0.174	−0.151	0.510	C(21)H	0.687	0.315	−0.306
C(22)H	0.246	−0.266	0.575	C(22)H	0.678	0.535	−0.302
C(23)H	0.310	−0.248	0.511	C(23)H	0.610	0.621	−0.268
C(24)H	0.302	−0.114	0.381	C(24)H	0.552	0.487	−0.239

[a] A C–H distance of 1.00 Å and for atoms C(7)–C(12) a tetrahedral geometry was assumed. This C–H distance is about 0.1 Å shorter than the spectroscopic value and is typical of values found in direct X-ray determinations.

The positional and thermal parameters for all atoms, obtained from the last cycle of refinement, are listed in Tables 1 and 2, together with the associated standard deviations as estimated from the inverse matrix. In Table 3 are listed the idealized

positional coordinates for all hydrogen atoms. Table 4* presents the values of 10 $|F_o|$ and 10 $|F_c|$ for those reflections used in the refinements.

DESCRIPTION OF THE STRUCTURE

The crystal structure consists of the packing of discrete molecules. All intermolecular contacts are normal, the shortest being 1.84 Å between C(12)H and C(12)H in adjacent symmetry-related molecules. There are two independent molecules in the asymmetric unit, and these are referred to as molecule 1 and molecule 2. Fig. 1 presents a drawing of molecule 2 and indicates the numbering scheme. The same numbering scheme is used for molecule 1 but no drawing of it is presented since both molecules have essentially the same structure. The figure displays the 50% probability ellipsoids for thermal motion, and Table 5 lists the root-mean-square amplitudes of vibration. The thermal vibrations of molecule 1, though differing somewhat from those of molecule 2, show the same overall features.
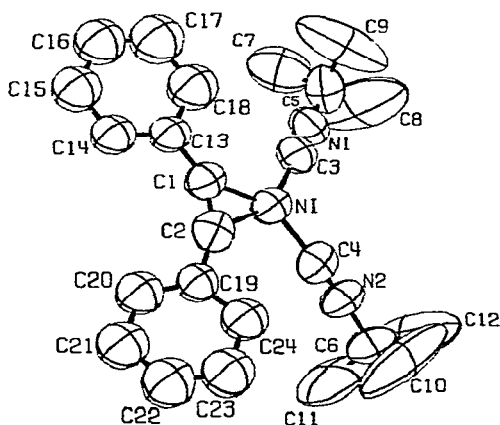
Fig. 1.

Relevant interatomic distances and angles for the two molecules are presented in Tables 6 and 7. Table 8 presents data on various relevant dihedral angles and vector-plane normal angles. The calculated least-squares planes through various atoms are listed in Table 9.

Generally speaking, the geometrical features of the two independent molecules do not differ significantly, and so average values will be used in the ensuing discussion unless we specifically remark to the contrary. The standard deviations associated with these average values are those of a single observation from the mean. They were derived by taking the larger of the estimates from the inverse matrix or

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TABLE 5

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Minimum	Intermediate	Maximum
Molecule 1			
Ni	0.210(3)	0.249(3)	0.277(3)
N(1)	0.243(16)	0.264(13)	0.306(13)
N(2)	0.243(16)	0.269(15)	0.339(13)
C(1)	0.180(18)	0.258(15)	0.282(16)
C(2)	0.174(20)	0.248(15)	0.278(14)
C(3)	0.240(16)	0.248(19)	0.295(16)
C(4)	0.198(20)	0.282(18)	0.322(17)
C(5)	0.176(25)	0.270(17)	0.372(18)
C(6)	0.230(21)	0.357(20)	0.381(19)
C(7)	0.244(23)	0.356(21)	0.676(28)
C(8)	0.249(23)	0.338(22)	0.767(30)
C(9)	0.255(22)	0.347(21)	0.625(25)
C(10)	0.285(23)	0.419(24)	0.686(29)
C(11)	0.226(24)	0.391(22)	0.668(28)
C(12)	0.288(26)	0.415(28)	0.934(44)
Molecule 2			
Ni	0.262(3)	0.300(3)	0.34 (3)
N(1)	0.284(19)	0.330(18)	0.383(15)
N(2)	0.276(17)	0.310(14)	0.375(14)
C(1)	0.267(17)	0.295(18)	0.339(17)
C(2)	0.235(17)	0.316(18)	0.346(19)
C(3)	0.288(17)	0.312(12)	0.340(20)
C(4)	0.241(18)	0.321(19)	0.347(17)
C(5)	0.307(24)	0.418(28)	0.429(26)
C(6)	0.288(26)	0.383(22)	0.411(21)
C(7)	0.330(26)	0.543(31)	0.588(32)
C(8)	0.318(29)	0.469(33)	0.964(51)
C(9)	0.334(27)	0.513(31)	0.815(43)
C(10)	0.245(26)	0.469(26)	0.878(41)
C(11)	0.255(29)	0.499(29)	0.746(35)
C(12)	0.284(29)	0.409(28)	0.981(44)

from the averaging of assumed equivalent quantities. Generally the latter estimate is a factor of two larger than that from the inverse matrix. We do not consider this to be an indication necessarily of significant differences between these quantities in the two molecules. It is more probable that the estimates from the inverse matrix are too small as a result of inadequacies in the model*.

In each molecule, the nickel atom is three-coordinate if the acetylene is regarded as a monodentate ligand. The three ligands adopt the expected configuration coplanar with the metal atom. The planarity of the inner coordination sphere is

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* The C–C distances within the phenyl rings show a much greater variation than expected on the basis of the standard deviations estimated from the inverse matrix. Whether this is the result of large thermal motions of these atoms, or whether there is indeed a significant variation from D_{6h} symmetry within the rings is impossible to discern from the present data. Diffraction data collected at a low temperature are probably needed to resolve this point.

TABLE 6

SELECTED BOND DISTANCES (Å) IN $Ni(C_6H_5C\equiv CC_6H_5)[(CH_3)_3C-N\equiv C]_2$

Distance	Molecule 1	Molecule 2	Average[a]
Ni–C(1)	1.884(10)	1.902(13) ⎫	1.899(19)
Ni–C(2)	1.884(9)	1.924(14) ⎬	
C(1)–C(2)	1.276(12)	1.291(16)	1.284(16)
Ni–C(3)	1.808(12)	1.862(15) ⎫	1.832(28)
Ni–C(4)	1.808(12)	1.850(15) ⎬	
C(3)–N(1)	1.166(12)	1.110(15) ⎫	1.142(24)
C(4)–N(2)	1.151(13)	1.141(14) ⎬	
N(1)–C(5)	1.470(14)	1.383(23) ⎫	1.442(44)
N(2)–C(6)	1.480(15)	1.433(18) ⎬	
C(5)–C(7)	1.440(18)	1.413(28) ⎫	
C(5)–C(8)	1.453(19)	1.324(29) ⎪	
C(5)–C(9)	1.427(18)	1.487(29) ⎪	1.44(5)
C(6)–C(10)	1.424(22)	1.476(24) ⎬	
C(6)–C(11)	1.486(24)	1.384(26) ⎪	
C(6)–C(12)	1.486(24)	1.483(23) ⎭	
C(1)–C(13)	1.474(14)	1.449(17) ⎫	1.453(31)
C(2)–C(19)	1.399(13)	1.456(17) ⎬	
C(13)–C(14)	1.397(14)	1.360(15) ⎫	
C(14)–C(15)	1.393(17)	1.400(17) ⎪	
C(15)–C(16)	1.352(18)	1.361(18) ⎪	
C(16)–C(17)	1.335(16)	1.367(20) ⎪	
C(17)–C(18)	1.412(15)	1.457(20) ⎪	
C(18)–C(13)	1.374(13)	1.389(17) ⎬	1.38(16)
C(19)–C(20)	1.342(19)	1.335(16) ⎪	
C(20)–C(21)	1.477(24)	1.443(19) ⎪	
C(21)–C(22)	1.292(23)	1.328(19) ⎪	
C(22)–C(23)	1.282(22)	1.316(18) ⎪	
C(23)–C(24)	1.467(23)	1.448(17) ⎪	
C(24)–C(19)	1.351(17)	1.390(16) ⎭	

Non-bonded distances

C(1)...C(3)	3.010(15)	3.063(20) ⎫	3.002(40)
C(2)...C(4)	2.908(16)	3.024(20) ⎬	
C(1)...C(14)	2.474(16)	2.462(20) ⎫	
C(1)...C(18)	2.489(16)	2.446(21) ⎪	
C(2)...C(20)	2.404(21)	2.434(21) ⎬	2.444(31)
C(2)...C(24)	2.401(22)	2.438(21) ⎭	
C(1)...C(24)	3.651(22)	3.694(20) ⎫	3.710(48)
C(2)...C(18)	3.763(16)	3.729(23) ⎬	
C(1)...C(20)	3.255(23)	3.354(21) ⎫	3.299(41)
C(2)...C(14)	3.284(16)	3.301(20) ⎬	

[a] These are the average quantities for the two independent molecules in the asymmetric unit. The estimated standard deviation in parentheses is the larger of an individual standard deviation or of the standard deviation of a single observation as calculated from the mean.

indicated by a small dihedral angle of about 2.6(7)° between the NiCC(of acetylene) and NiCC(of t-butyl isocyanide) planes, and independently by a maximum displacement of 0.07 Å from the least-squares plane through these atoms. The angles C(1)–Ni–C(2), C(1)–Ni–C(3), C(3)–Ni–C(4), and C(2)–Ni–C(4) average 39.5(5), 109.1(5),

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C(5)–C(7)	1.440(18)	1.413(28) ⎱	
C(5)–C(8)	1.453(19)	1.324(29)	
C(5)–C(9)	1.427(18)	1.487(29)	1.44(5)
C(6)–C(10)	1.424(22)	1.476(24)	
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C(1)–C(13)	1.474(14)	1.449(17) ⎱	1.453(31)
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C(16)–C(17)	1.335(16)	1.367(20)	
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C(18)–C(13)	1.374(13)	1.389(17)	1.38(16)
C(19)–C(20)	1.342(19)	1.335(16)	
C(20)–C(21)	1.477(24)	1.443(19)	
C(21)–C(22)	1.292(23)	1.328(19)	
C(22)–C(23)	1.282(22)	1.316(18)	
C(23)–C(24)	1.467(23)	1.448(17)	
C(24)–C(19)	1.351(17)	1.390(16)	

Non-bonded distances

C(1)...C(3)	3.010(15)	3.063(20) ⎱	3.002(40)
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C(1)...C(14)	2.474(16)	2.462(20) ⎱	
C(1)...C(18)	2.489(16)	2.446(21)	
C(2)...C(20)	2.404(21)	2.434(21)	2.444(31)
C(2)...C(24)	2.401(22)	2.438(21) ⎰	
C(1)...C(24)	3.651(22)	3.694(20) ⎱	3.710(48)
C(2)...C(18)	3.763(16)	3.729(23) ⎰	
C(1)...C(20)	3.255(23)	3.354(21) ⎱	3.299(41)
C(2)...C(14)	3.284(16)	3.301(20) ⎰	

[a] These are the average quantities for the two independent molecules in the asymmetric unit. The estimated standard deviation in parentheses is the larger of an individual standard deviation or of the standard deviation of a single observation as calculated from the mean.

indicated by a small dihedral angle of about 2.6(7)° between the NiCC(of acetylene) and NiCC(of t-butyl isocyanide) planes, and independently by a maximum displacement of 0.07 Å from the least-squares plane through these atoms. The angles C(1)–Ni–C(2), C(1)–Ni–C(3), C(3)–Ni–C(4), and C(2)–Ni–C(4) average 39.5(5), 109.1(5),

TABLE 8

INTRA-PLANAR AND VECTOR-PLANE-NORMAL ANGLES (°) IN $Ni(C_6H_5C\equiv CC_6H_5)[(CH_3)_3C-N\equiv C]_2$

Angle	Molecule 1	Molecule 2
Dihedral angles[a]		
Ni, C(2), C(1) ⎫ Ni, C(3), C(4) ⎭	2.8(7)	2.4(7)
C(3), Ni, C(1) ⎫ C(4), Ni, C(2) ⎭	178.4(4)	177.8(6)
Phenyl 1 [C(13), C(15), C(17)] ⎫ Phenyl 2 [C(19), C(21), C(23)] ⎭	43.7(8)	22.2(7)
C(1), C(2), C(19) ⎫ Phenyl 2 [C(19), C(21), C(23)] ⎭	29.3(19)	31.2(26)
C(2), C(1), C(13) ⎫ Phenyl 1 [C(13), C(15), C(17)] ⎭	6.0(18)	15.0(23)
C(1), C(2), C(19) ⎫ C(2), C(1), C(13) ⎭	169.4(32)	174.4(42)
Ni, C(1), C(2) ⎫ C(1), C(2), C(13) ⎭	174.4(18)	177.9(26)
Ni, C(2), C(1) ⎫ C(2), C(1), C(19) ⎭	175.0(18)	176.5(25)
Vector-Plane-Normal angles[b]		
C(1)–C(2) ⎫ Ni, C(3), C(4) ⎭	87.2(7)	88.3(6)
C(1)–C(13) ⎫ Phenyl 1 [C(13), C(15), C(17)] ⎭	93.2(8)	91.9(10)
C(2)–C(19) ⎫ Phenyl 2 [C(19), C(21), C(23)] ⎭	91.5(9)	90.3(10)

[a] Let the two groups of atoms be A(1)–A(2)–A(3) and B(1)–B(2)–B(3). Form vector $V(1)$ from A(1) to A(2). Form vector $V(2)$ from A(1) to A(3). Then the normal to the plane of A(1)–A(2)–A(3) is parallel to $V(1) \times V(2)$. Form a similar normal to the plane of B(1)–B(2)–B(3). Then the dihedral angle is defined as an angle between these two normals. [b] Let the two groups of atoms be A(1)–A(2) and B(1)–B(2)–B(3). Form the vector $V(1)$ from A(1) to A(2). Form the normal $V(2)$ to B(1)–B(2)–B(3) as for the dihedral angles. Then the angle given here is between $V(1)$ and $V(2)$.

The nickel atom is equidistant from the acetylenic carbon atoms in each of the two independent molecules in the asymmetric unit. The average Ni–C distance is 1.899(19) Å, and this value is identical with the Ni–C (of acetylene) distance in the bridging acetylene–nickel complex, $[(\pi C_5H_5)Ni]_2(C_6H_5C\equiv CC_6H_5)^9$. In the present structure, the Ni–C≡C angles average 70.2(9)°. The central atoms of the acetylene lie very nearly in the plane defined by the Ni atom and the two C–N≡C groups, there being no tilt similar to the 10° angle between C≡C and PtP₂ in the complex Pt-$(C_6H_5C\equiv CC_6H_5)[P(C_6H_5)_3]_2$.

The coordinated acetylene is no longer linear but displays a *cis*-geometry with the phenyl rings bent at angles of about 148.5° from the C(1)≡C(2) bond axis. There is also some lengthening of the C≡C bond upon coordination; the average

TABLE 9

WEIGHTED LEAST-SQUARES PLANES

Plane equation: $Ax + By + Cz - D = 0$ with x, y, z in monoclinic coordinates.

MOLECULE 1

Plane no.	A	B	C	D (Å)
1	11.623	−8.290	−9.124	−0.273
2	15.578	−6.704	−10.814	0.214
3	5.873	8.233	7.957	3.888
4	15.566	−6.699	−10.824	0.212
5	4.781	8.647	7.565	3.412

DEVIATIONS FROM THE PLANES (in Å) OF ATOMS USED TO DETERMINE THE PLANES

Atom	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
Ni	0.0002(2)				
N(1)	−0.010(9)				
N(2)	0.011(10)				
C(1)	−0.032(9)	0.024(9)		0.022(9)	−0.127(9)
C(2)	0.041(10)		0.002(10)	0.001(10)	0.125(10)
C(3)	−0.018(11)				
C(4)	0.007(12)				
C(5)	0.041(13)				
C(6)	−0.045(17)				
C(13)		−0.035(10)		−0.036(10)	
C(14)		−0.003(12)		−0.004(12)	
C(15)		−0.008(15)		−0.008(15)	
C(16)		0.033(14)		0.035(14)	
C(17)		0.003(12)		0.005(12)	
C(18)		−0.009(11)		−0.009(11)	
C(19)			−0.000(10)		0.056(10)
C(20)			0.011(16)		−0.020(16)
C(21)	61		−0.061(21)		−0.163(21)
C(22)			0.065(17)		−0.013(17)
C(23)			−0.059(22)		−0.058(22)
C(24)			0.011(17)		0.084(17)

C≡C distance of 1.284(16) Å can be compared with the bond length of 1.19(2) Å reported[22] for free diphenylacetylene in the solid state. The C≡C–C(phenyl) distances average 1.453(31) Å and are similar to corresponding distances in other diphenyl-acetylene complexes[6,9]. The average C≡C–C(phenyl) and Ni–C(acetylene–C(phenyl) angles of 148.6(1.4) and 141.3(1.1) are also reasonable.

There is a considerable dihedral angle between the planes of the phenyl rings of the coordinated diphenylacetylene unit. This angle in 43.7(8)° for molecule 1 and 22.2(7)° for molecule 2, and the difference between molecules 1 and 2 here is probably the most significant variation in the detailed geometries of the two molecules in the asymmetric unit. Somewhat larger dihedral angles, with values in the range 49–75°, have been reported for the phenyl rings in other molecules incorporating the

MOLECULE 2

Plane no.	A	B	C	D (Å)
1	−2.814	4.318	13.576	−3.622
2	6.711	4.291	11.759	1.854
3	6.757	0.065	12.966	0.699
4	6.589	4.136	11.884	1.785
5	7.340	0.435	12.794	1.252

DEVIATIONS FROM THE PLANES (in Å)

Atom	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
Ni	0.008(2)				
N(1)	−0.046(12)				
N(2)	−0.040(11)				
C(1)	−0.035(12)	−0.024(12)		−0.068(12)	0.141(12)
C(2)	−0.072(11)		−0.023(11)	0.056(11)	−0.124(11)
C(3)	0.012(14)				
C(4)	0.015(12)				
C(5)	−0.035(20)				
C(6)	−0.041(20)				
C(13)		0.012(12)		−0.011(12)	
C(14)		0.028(13)		0.010(13)	
C(15)		−0.022(14)		−0.019(14)	
C(16)		−0.015(16)		0.006(15)	
C(17)		0.006(17)		0.025(17)	
C(18)		0.012(16)		0.008(16)	
C(19)			−0.007(12)		−0.055(12)
C(20)			0.042(13)		0.038(13)
C(21)			−0.013(15)		0.036(15)
C(22)			−0.045(16)		0.008(16)
C(23)			0.017(16)		0.028(16)
C(24)			0.021(14)		−0.020(14)

coordinated diphenylacetylene unit. Two components of the dihedral angle can be recognized in the following angles for the present structure: (1) The dihedral angle between the C(2)–C(1)–C(13) plane and the plane of the phenyl ring [C(13)–C(15)–C(17)] is 6.0(18) and 15.0(23) for molecules 1 and 2 respectively while the related angle between the C(1)–C(2)–C(19) plane and the plane of the phenyl ring [(C(19)–C(21)–C-(23)] is 29.3(19) and 31.2(26)° for molecules 1 and 2, respectively. These angles would be 0° if the diphenylacetylene unit were strictly planar, and the deviations from 0° represent the extent of rotation of the phenyl rings about the acetylenic-C to phenyl-C bond axis. (2) There is then a small "tilt" angle of 10.6(32)° and 5.6(42)° for molecules 1 and 2 respectively between the two C≡C–C(phenyl) planes. The rotation and tilting of the phenyl rings presumably result (at least in part) from attempts to relieve steric
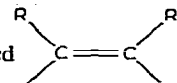
strain imposed by short non-bonded contacts between C(1)...C(20) and C(2)...C(14). These non-bonded distances are all close to 3.3 Å in the present structure.

DISCUSSION

Table 10 compares the C≡C bond length and R–C≡C bond angle data for the present complex with corresponding data for several other M(RC≡CR) complexes. There is some variation in both parameters from compound to compound, and a rough correlation between the lengthening of the C≡C bond and the deviation of the R–C≡C bond angle from linearity is apparent. Consideration of other relevant structural data reveals that the acetylene unit is more perturbed in bridging-acetylene complexes. For instance, C≡C bond distances of 1.35(3) and 1.46 Å are reported for the complexes [(πC₅H₅)Ni]₂(C₆H₅C≡CC₆H₅)[9] and [(CO)₃Co]₂(C₆H₅C≡CC₆H₅)[6], respectively. These observations can be rationalized in terms of the ligand interacting simultaneously with two metal atoms in the latter two complexes. Perhaps the most noteworthy feature of the tabulated data is the generally large value of the errors associated with most parameters. As a result, it is impossible to comment with any confidence on the finer details of the bonding of acetylenes to transition metals. Notwithstanding this, it is possible to draw some general conclusions that may stimulate the pursuit of a better understanding of the nature of coordinated acetylenes.

TABLE 10

GEOMETRY OF UNCOORDINATED AND COORDINATED ACETYLENES

Acetylene	Ref.	C≡C distance (Å)	R–C≡C angle (°)
Uncoordinated RC≡CR	22	1.202(5)ᵃ	180
PtCl₂[(CH₃)₃CC≡CC(CH₃)₃] (p-toluidine)	2	1.24(2)	162, 165(1)
Nb(π-C₅H₅)(CO)(C₆H₅C≡CC₆H₅)[π-C₄(C₆H₅)₄]	5	1.26(4)	142(3)
Ni(C₆H₅C≡CC₆H₅)[(CH₃)₃C–N≡C]₂	This work	1.28(2)	149(1)
Pt(C₆H₅C≡CC₆H₅)[P(C₆H₅)₃]₂	3	1.32(9)	140
Nb(π-C₅H₅)(CO)(C₆H₅C≡CC₆H₅)₂	4	1.35(2)	138(4)
Uncoordinated (C=C with R groups)	22	1.339(2)	117.3(3)

ᵃ An early study[23] of the solid state structure of diphenylacetylene gives a C≡C distance of 1.19(2) Å and an R–C≡C angle of 180(2)°.

Several discussions of the preferred configuration of olefin and acetylene complexes of the Group VIII transition metals have emerged from recent investigations of these complexes. For square-planar complexes such as Zeise's salt[24], [PtCl₃(C₂H₄)]⁻ and PtCl₂[(CH₃)₃CC≡CC(CH₃)₃](p-toluidine)[2], it is now apparent that the olefin or acetylene adopts a configuration normal to the plane through the metal atom, the midpoint of the carbon–carbon unsaturated bond, and the donor atoms of the three other ligands. This configuration may be forced on the system by steric requirements[1] but is also reasonable in terms of available bonding models[25–27]. It has been pointed out that the olefin or acetylene to transition metal interaction in such

complexes is not rigorously symmetrical. For example, in the complex $PtCl_2[(CH_3)_3$-$CC\equiv CC(CH_3)_3](p$-toluidine)[2], the acetylenic bond makes an angle of $85.2°$ rather than $90°$ with the coordination plane and its mid-point lies 0.10 Å above the coordination plane; there is then a small difference in the two Pt–C distances. This type of distortion may be fairly general[28] but an explanation of the effect is not available. With trigonal complexes such as $Pt(C_6H_5C\equiv CC_6H_5)[P(C_6H_5)_3]_2$[3] and $Ni[(CN)_2$-$C\equiv C(CN)_2][(CH_3)_2C–C\equiv N]_2$[12], there appears to be no steric limitation on the disposition of the C–C system relative to the plane of the rest of the molecule so that planar and pseudo-tetrahedral configurations are both sterically reasonable. Moreover, theoretical treatments are available to account for both the planar[27] and the twisted[29] sterochemistry although there is a need to define the twist precisely[12]. Structural data on trigonal olefin[1] and acetylene[3] complexes have generally revealed a significant distortion from ideal planarity. In the complex $Pt(C_6H_5C\equiv CC_6H_5)$-$[P(C_6H_5)_3]_2$[3] for instance, the platinum, the two phosphorus atoms, and one acetylenic carbon atom lie in a plane with the line of the two acetylenic carbon atoms making an angle of about $14°$ with the plane. However, in the two independent molecules of the present complex, $Ni(C_6H_5C\equiv CC_6H_5)[(CH_3)_3C–N\equiv C]_2$, there are no indications of asymmetry in the C≡C to Ni linkage. Thus the Ni–C(1) and Ni–C(2) distances are $1.88(1)$ and $1.88(1)$ Å respectively for molecule 1 and $1.90(1)$ and $1.92(1)$ Å respectively for molecule 2, while the dihedral angle between the Ni–CC(of acetylene) and Ni–CC-(of tert-butyl isocyanide) planes is only $2.8(7)$ and $2.4(7)°$ for molecules 1 and 2, respectively. There is however alternative evidence of asymmetry in the sense that the two phenyl rings in each diphenylacetylene unit are rotated to different extents about the acetylenic carbon to phenyl carbon bond.

The usual description of olefin–metal bonding[30,31] can be extended, with only slight modification, to acetylene–transition metal systems[25–27]. Thus, if we assume a planar, trigonal configuration for a complex $M(C_6H_5C\equiv CC_6H_5)L_2$, the bond description would include forwards donation from the filled C≡C π_{xy} orbital to a vacant dp^2 hybrid orbital $(d_{xy}+p_x+p_y)$ on nickel supported by back-donation from a filled $d_{x^2-y^2}$ orbital on the metal to the unoccupied $C\equiv C\pi^*_{xy}$ orbital. The bond description for acetylenes (but not for olefins) can be extended because acetylenes possess an additional set of π,π^* orbitals orthogonal to the $M–C_2$ plane. Consequently, it is possible to add further bonding interactions where the filled acetylene π_z orbital overlaps with a metal d^2 hybrid $(d_{xz}+d_{yz})$ and the $(d_{xz}-d_{yz})$ metal orbital overlaps with the unoccupied π^*_z orbital of the acetylene. A recent molecular orbital calculation[27] indicates that a contribution from this latter interaction could be significant, and it can be argued that this should serve to stabilize the M–C bonding over that found in comparable olefin–metal complexes.

However, indirect evidence from spectroscopic studies[14] seems to indicate that $C_6H_5C\equiv CC_6H_5$ is more weakly bound to Ni and Pd in the complexes $M[(CH_3)_3$-$C–N\equiv C]_2L$ than are such ligands as fumaronitrile, azobenzene, molecular oxygen, and tetracyanoethylene. Moreover, the chemical behavior of $M(C_6H_5C\equiv CC_6H_5)$-$[(CH_3)_3C–N\equiv C]_2$ complexes indicates that the acetylene unit is very labile. Thus, the diphenylacetylene in solutions of $Ni(C_6H_5C\equiv CC_6H_5)[(CH_3)_3C–N\equiv C]_2$ can be isolated from solution only when excess diphenylacetylene is present[32]. These observations seem to work against the idea of increased stability through out-of-plane bonding interactions for acetylene–transition metal systems.

The limited amount of structural data that is available on the group of complexes $Ni[(CH_3)_3C-N\equiv C]_2L$, where L is an unsaturated organic ligand such as tetracyanoethylene, azobenzene, or diphenylacetylene, is confusing when considered in relation to the alternative claims of theory and experiment. One indication of the extent of L-to-M interaction in these complexes might be the change in the C–C or N–N distance upon coordination. On this basis, we would predict a very strong interaction for the tetracyanoethylene and azobenzene complexes, where the C=C and N=N bond distances are lengthened by 0.14 and 0.15 Å respectively from the values for the free ligands, and a much weaker interaction in the diphenylacetylene complex where the corresponding lengthening of the C≡C bond is only 0.08 Å. This conclusion is consistent with the chemical evidence cited earlier. However, we can also assume a correlation between bond length and bond strength and then use differences in the Ni–C (or Ni–N) distances as an indication of the relative strengths of the metal–ligand interactions. Using this criterion, we would suggest that the acetylene- and azobenzene-to-metal interactions are stronger than that for the olefin–metal system since the appropriate distances are 1.90, 1.90, and 1.95 Å for the diphenylacetylene, azobenzene, and tetracyanoethylene complexes, respectively. The observations here are in satisfactory agreement with the theoretical predictions[27].

There is an obvious need for a continuation of systematic structural studies on complexes such as these, and data on isostructural *cis*-stilbene and diphenylacetylene complexes, or on isostructural fumaronitrile and dicyanoacetylene complexes, would be most instructive.

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