The Structure of Bis(*t*-butyl isocyanide)(tetracyanoethylene)nickel(0), $Ni((CN)_2C{=}C(CN)_2)((CH_3)_3C{-}N{\equiv}C)_2$

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Abstract: The structure of bis(*t*-butyl isocyanide)(tetracyanoethylene)nickel(0), $Ni((CN)_2C{=}C(CN)_2)((CH_3)_3C{-}N{\equiv}C)_2$, has been determined at room temperature from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final *R* factor on *F* of 3.6%, based on 1725 observations above background. The material crystallizes in space group C_{2h}^5-$P2_1/c$ of the monoclinic system, with four molecules in a cell of dimensions a = 10.409 (8), b = 10.159 (8), c = 19.342 (14) Å, β = 112.33 (3)°. The observed and calculated densities are 1.24 (1) and 1.239 g/cm^3, respectively. If one counts the tetracyanoethylene as a single ligand, the coordination about the Ni atom is approximately trigonal. The *t*-butyl isocyanide ligands have their expected geometry, and the average Ni–C distance is 1.866 (5) Å. The central two atoms of the tetracyanoethylene ligand are equidistant from the metal, with an average Ni–C bond length of 1.954 (4) Å. The $C(CN)_2$ portions of the ligand remain planar, and the angle between the central C–C bond and the normals to the planes formed by these portions is 61.6 (5)°. The central C–C bond is 1.476 (5) Å, 0.137 (9) longer than that of 1.339 (8) Å in tetracyanoethylene, and concomitant with this lengthening the tetracyanoethylene ligand is nonplanar with the $C(CN)_2$ groups bent away from the Ni atom. A simple correlation has been found between this bending angle and the increase of the central bond over the value in the free ligand. The central C–C vector is not coplanar with the plane formed by the Ni and the two bonding C atoms of the *t*-butyl isocyanide groups, but rather makes an angle of 82.2 (2)° with the normal to this plane. Alternatively, the angle between the normal to this plane and the normal to the plane formed by the Ni atom and the two central atoms of the tetracyanoethylene ligand is 23.9 (2)°. The Ni atom lies above and the four C atoms lie below the least-squares plane through these five atoms.

Although Zeise's salt was the first example of an organometallic complex, there exists a paucity of accurate data on the structural features of the bonding of olefins to transition metals.[1] In recent years there has been considerable interest in oxidative addition reactions,[2-4] especially in relation to homogeneous catalysis, and a number of new, crystallizable transition metal–olefin complexes have been prepared and characterized. Among such complexes are the triangular type formed by the addition of the olefin to the L_2M species, where L is generally a phosphine[5] and M is Ni, Pd, or Pt. Recently Otsuka, Nakamura, and Tatsuno[6] described analogous complexes where L is *t*-butyl isocyanide. The present structural investigation is the first on compounds of this series.

Our motivation for the present study is not only to provide comparative data on metal–olefin bonding, but also to provide data that are potentially useful for understanding the mode of attachment of other small molecules, especially molecular oxygen,[7] to these same metal systems.

Experimental Section

Unit Cell and Space Group. The crystals of Ni(TCNE)(*t*-BuNC)$_2$ (TCNE = tetracyanoethylene, *t*-BuNC = *t*-butyl isocyanide) used in this study were kindly supplied by Professor S. Otsuka. Preliminary optical and X-ray studies of the crystals indicated monoclinic symmetry. Precession photographs taken with Mo Kα radiation of the 0*kl*, 1*kl*, *h*0*l*, and *h*1*l* nets showed systematic absences 0*k*0 for *k* odd and *h*0*l* for *l* odd, characteristic of space group C_{2h}^5-$P2_1/c$. The cell dimensions, obtained with Mo Kα_1 radiation (λ 0.7093 Å) at 25° from refinement of the setting angles of 15 reflections centered on a four-circle diffractometer,[8] are a = 10.409 (8), b = 10.159 (8), c = 19.342 (14) Å, β = 112.33 (3)°. An observed density of 1.24 (1) g/cm^3, obtained by flotation in ($F_2ClCCCl_2F$)–hexane solutions, agrees well with that of 1.239 g/cm^3 calculated for four formula units in the cell. Thus no crystallographic symmetry conditions need be imposed on the molecules.

Collection and Reduction of Intensity Data. Intensity data were collected with Mo Kα radiation from a crystal of octagonal prismatic habit of approximate dimensions 0.2 mm along c^* (the prism axis) and 0.3 mm in diameter. The methods used for collection of the diffractometer data parallel those previously described.[8,9] A unique data set was first collected out to 2θ (Mo Kα_1) = 40°. A subsequent collection from 40 to 44° yielded relatively few intensities above background and so data collection was terminated. Of the total of 2320 independent reflections examined, 1725 obeyed the condition $F_o^2 > 3\sigma(F_o^2)$, and these we describe as being above background. Only these reflections were used in subsequent calculations. The intensities of four standard reflections, monitored during the data collection, stayed constant to within 2%.

These data were collected by the θ–2θ scan technique. Reflections were scanned at 1° in 2θ per minute from −0.45 to +0.55° from the Mo Kα_1 maximum. The diffracted beams were filtered through 3.0-mil Nb foil. Background counts of 10 sec each were taken at each end of the scan range. The counter was placed 31 cm from the crystal and was preceded by an aperture of dimensions 4.0 × 4.0 mm. The pulse-height analyzer was set to admit 90% of the Mo Kα peak. The takeoff angle was 1.3°. When necessary, the diffracted beams were attenuated by Cu foil to prevent coincidence losses. The data were processed in the manner previously described[8,9] to yield values of F_o^2 and $\sigma(F_o^2)$. A value of p of 0.04 was used in the estimation of the standard deviations.

Solution of the Structure. The structure was readily solved by the usual combination of Patterson, Fourier, and least-squares methods.[10] In the least-squares calculations the function $\Sigma W\cdot$

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Table I. Positional and Thermal Parameters for $Ni((CN)_2C{=}C(CN)_2)((CH_3)_3C{-}N{\equiv}C)_2$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.10067 (5)[b]	0.15564 (6)	0.22178 (3)	71.9 (7)	94.4 (7)	22.1 (2)	−3.7 (6)	17.2 (3)	−1.1 (3)
N(1)	−0.1171 (4)	0.1683 (4)	0.0659 (2)	115 (5)	100 (5)	24 (1)	−4 (4)	17 (2)	−6 (2)
N(2)	0.3447 (4)	0.2311 (4)	0.1836 (2)	88 (5)	85 (4)	30 (1)	−2 (4)	27 (2)	−1 (2)
N(3)	0.2868 (5)	−0.0089 (5)	0.4102 (3)	215 (8)	146 (7)	40 (2)	74 (6)	20 (3)	21 (3)
N(4)	0.3006 (5)	0.4074 (5)	0.3731 (3)	144 (7)	126 (6)	69 (3)	−44 (6)	10 (3)	−17 (3)
N(5)	−0.1271 (5)	0.0057 (5)	0.3204 (3)	196 (8)	99 (6)	70 (3)	−37 (5)	77 (4)	−4 (3)
N(6)	−0.0969 (4)	0.4246 (4)	0.2740 (2)	106 (5)	77 (5)	41 (2)	17 (4)	23 (2)	3 (2)
C(1)	−0.0372 (5)	0.1643 (4)	0.1258 (3)	98 (6)	82 (5)	25 (2)	−6 (5)	22 (3)	−5 (3)
C(2)	−0.2126 (5)	0.1728 (6)	−0.0124 (2)	128 (7)	148 (7)	21 (2)	16 (6)	8 (3)	−4 (3)
C(3)	0.2545 (5)	0.1935 (4)	0.1982 (2)	97 (6)	63 (5)	26 (2)	3 (4)	23 (3)	−3 (2)
C(4)	0.4504 (5)	0.2984 (4)	0.1639 (3)	93 (6)	83 (5)	40 (2)	−13 (5)	34 (3)	1 (3)
C(5)	0.0141 (4)	0.1931 (4)	0.2935 (2)	78 (5)	47 (5)	26 (2)	1 (4)	21 (2)	0 (2)
C(6)	0.1671 (4)	0.1889 (4)	0.3290 (2)	77 (5)	68 (5)	23 (2)	0 (4)	15 (2)	1 (2)
C(7)	0.2324 (5)	0.0781 (5)	0.3745 (3)	116 (7)	110 (7)	25 (2)	29 (6)	16 (3)	0 (3)
C(8)	0.2409 (5)	0.3107 (5)	0.3532 (3)	87 (6)	105 (7)	34 (2)	9 (5)	12 (3)	0 (3)
C(9)	−0.0647 (5)	0.0886 (5)	0.3083 (3)	121 (7)	66 (5)	37 (2)	2 (5)	38 (3)	−5 (3)
C(10)	−0.0505 (4)	0.3209 (5)	0.2822 (2)	75 (5)	84 (6)	25 (2)	−8 (4)	17 (2)	−3 (2)
C(11)	−0.3557 (6)	0.1922 (8)	−0.0151 (4)	138 (8)	319 (14)	45 (3)	29 (9)	6 (4)	−25 (5)
C(12)	−0.2001 (9)	0.0471 (8)	−0.0483 (4)	355 (16)	271 (14)	45 (3)	148 (12)	−20 (6)	−58 (5)
C(13)	−0.1686 (9)	0.2823 (10)	−0.0467 (4)	323 (17)	372 (18)	44 (3)	−56 (14)	23 (6)	62 (6)
C(14)	0.3798 (7)	0.3435 (8)	0.0841 (4)	169 (9)	306 (14)	66 (3)	−15 (10)	42 (5)	76 (6)
C(15)	0.5656 (6)	0.2039 (6)	0.1716 (4)	161 (9)	157 (9)	102 (4)	46 (7)	91 (5)	38 (5)
C(16)	0.5004 (8)	0.4128 (8)	0.2137 (5)	261 (13)	241 (12)	110 (5)	−150 (11)	115 (7)	−86 (6)

[a] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. The values of β have been multiplied by 10^4. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the less significant digits.

Table II. Idealized Positional Coordinates for Hydrogen Atoms[a]

Atom	x	y	z	Atom	x	y	z
C(11)H(1)	−0.3654	0.2813	0.0053	C(14)H(1)	0.2963	0.3996	0.0771
C(11)H(2)	−0.4264	0.1861	−0.0680	C(14)H(2)	0.4445	0.3938	0.0665
C(11)H(3)	−0.3798	0.1232	0.0157	C(14)H(3)	0.3453	0.2635	0.0494
C(12)H(1)	−0.2281	−0.0326	−0.0222	C(15)H(1)	0.5301	0.1236	0.1387
C(12)H(2)	−0.2590	0.0409	−0.1020	C(15)H(2)	0.6402	0.2456	0.1572
C(12)H(3)	−0.0998	0.0278	−0.0411	C(15)H(3)	0.6116	0.1716	0.2249
C(13)H(1)	−0.0632	0.2856	−0.0318	C(16)H(1)	0.5344	0.3859	0.2682
C(13)H(2)	−0.2130	0.2876	−0.1020	C(16)H(2)	0.5756	0.4625	0.2053
C(13)H(3)	−0.1908	0.3735	−0.0270	C(16)H(3)	0.4202	0.4790	0.2062

[a] A C–H distance of 1.00 Å and tetrahedral geometry were 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.

$(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and where the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for Ni, N, and C were taken from the usual tabulation,[11] while those for H were from the calculations of Stewart, *et al.*[12] The values of the anomalous terms, $\Delta f'$ and $\Delta f''$, were taken from the calculations of Cromer[13] and were included in F_c.[14]

The Ni atom position was found from a Patterson function. Refinement, followed by a difference Fourier synthesis, led to positions for all remaining nonhydrogen atoms. Isotropic refinement of this trial structure led to values of R_1 and R_2 of 0.081 and 0.099, respectively, where $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o)^{1/2}$. The data were next corrected for absorption effects. The ten crystal faces belong to the forms {010}, {001}, {100}, and {110}. On the basis of a calculated linear absorption coefficient of 10.32 cm^{-1}, the transmission factors were found to vary between 0.76 and 0.82. Three cycles of complete anisotropic least-squares refinement reduced R_1 and R_2 to 0.042 and 0.056. Subsequent difference Fourier synthesis in the separate planes where the hydrogen atoms of the methyl groups were expected led to reasonable positions for all 18 methyl hydrogen atoms. These positions were idealized on the assumption that C–H = 1.00 Å and ∠H–C–H = 109° 28′. The contributions from these idealized hydrogen atoms were added to subsequent structure factor calculations. A thermal parameter of 9.6 Å^2 was assigned to these hydrogen atoms, corresponding approximately to the average isotropic equivalent of the thermal parameters for the methyl carbon atoms. Two further cycles of anisotropic refinement for 208 variables and 1725 observations reduced the values of R_1 and R_2 to 0.036 and 0.043, respectively, and led to the final parameters given in Table I. The idealized positions of the hydrogen atoms are given in Table II. An analysis of $|F_o|$ and $|F_c|$ as a function of scattering angle, magnitude of $|F_o|$, and Miller indices revealed no unexpected trends and provided no evidence for extinction effects. The error in an observation of unit weight is 1.38. Thus the weighting scheme used appears to be a reasonable one. The maximum density on a final difference Fourier synthesis is 0.26 electron/Å^3, approximately 5% of the height of a C atom in this structure. A comparison of $|F_o|$ and $|F_c|$ for the 595 reflections omitted from the refinement ($F_o^2 < 3\sigma(F_o^2)$) revealed none in which $|F_o^2 - F_c^2| > 3.8\sigma(F_o^2)$. Thus these data are omitted from the tabulation of structure amplitudes (Table III) where we present the final values of $10|F_o|$ and $10|F_c|$ (in electrons) for those reflections used in the refinements.[15]

Description of the Structure

The crystal structure consists of the packing of monomeric molecules. All intermolecular contacts are

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(10) In addition to various local programs for the CDC-6400, local variations of the following programs were used in this study: GONO9 absorption program of W. C. Hamilton, FORDAP Fourier program of A. Zalkin, ORFFE error function program of W. R. Busing and H. A. Levy, and the ORTEP plotting program of C. Johnson. NUCLS, the least-squares program used, in its nongroup form resembles the Busing–Levy ORFLS program.

(11) J. A. Ibers, "International Tables for X-ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

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(15) This table has been deposited as Document No. NAPS-01002 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $2.00 for a microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

Table IV. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Inter	Max	Atom	Min	Inter	Max
Ni	0.1778 (9)	0.1903 (9)	0.2227 (8)	C(6)	0.188 (7)	0.189 (7)	0.198 (6)
N(1)	0.191 (6)	0.232 (6)	0.238 (5)	C(7)	0.200 (7)	0.207 (7)	0.271 (7)
N(2)	0.184 (6)	0.210 (6)	0.227 (5)	C(8)	0.197 (7)	0.235 (8)	0.254 (7)
N(3)	0.202 (7)	0.288 (6)	0.363 (6)	C(9)	0.177 (7)	0.208 (8)	0.258 (7)
N(4)	0.204 (7)	0.295 (6)	0.373 (7)	C(10)	0.183 (7)	0.200 (7)	0.215 (7)
N(5)	0.193 (7)	0.259 (6)	0.356 (6)	C(11)	0.231 (8)	0.297 (8)	0.426 (9)
N(6)	0.188 (7)	0.234 (6)	0.263 (5)	C(12)	0.208 (10)	0.286 (9)	0.559 (11)
C(1)	0.191 (7)	0.205 (7)	0.221 (7)	C(13)	0.217 (10)	0.372 (10)	0.502 (11)
C(2)	0.179 (7)	0.251 (7)	0.292 (7)	C(14)	0.217 (9)	0.287 (8)	0.466 (10)
C(3)	0.175 (7)	0.201 (7)	0.216 (6)	C(15)	0.206 (8)	0.264 (8)	0.425 (9)
C(4)	0.176 (7)	0.218 (7)	0.258 (6)	C(16)	0.223 (9)	0.291 (9)	0.505 (10)
C(5)	0.157 (8)	0.182 (7)	0.207 (6)				

normal, the shortest being 2.16 Å between C(12)H(3) atoms in adjacent molecules.

Figure 1 presents a drawing of the molecule and indicates the numbering scheme. Figure 1 also displays the vibrational thermal ellipsoids. Table IV presents the root-mean-square amplitudes of vibration. These vibrational data appear to be reasonable; as expected, the methyl carbon atoms exhibit the greatest thermal motion. Table V presents relevant bond distances and angles.

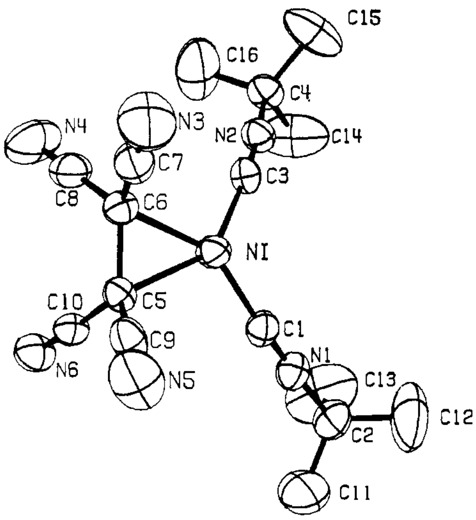

Figure 1. A drawing of the $Ni((CN)_2C{=}C(CN)_2)((CH_3)_3C{-}N{\equiv}C)_2$ molecule. Hydrogen atoms have been omitted. The 50% probability vibrational ellipsoids are shown.

The Ni atom has its expected trigonal coordination where we consider the TCNE molecule as a single ligand. The average Ni–C distance for the *t*-BuNC groups of 1.866 (5) Å is the same as that of 1.862 (6) Å for the basal Ni–C distances in the $Ni(CN)_5^{3-}$ ion.[16] The average C≡N and N—C distances in the C≡N—C fragment are 1.143 (5) and 1.463 (6) Å, respectively, whereas they are 1.14 (2) and 1.44 (3) Å in pentakis(methyl isocyanide)cobalt(I) perchlorate.[17] In both instances the C≡N—C fragment is very nearly linear. The small deviations from linearity in the present structure perhaps result from packing forces. The $C{-}CH_3$ distances, which average 1.483 (18) Å, are somewhat shorter than expected, but such shortening is probably apparent, rather than real, and is the result of vibrational effects.

The Ni–C distances to the TCNE molecule average 1.954 (4) Å and are not significantly different. These distances are in the range of the Ni–C distances of 1.93 and 2.01 (2) Å for the two determinations[18,19] of the structure of $Ni(C_2H_4)(P(C_6H_5)_3)_2$. Because of the lack of agreement between these two somewhat imprecise determinations, it is not possible to ascertain if the Ni–C distances differ significantly in the ethylene and TCNE complexes.

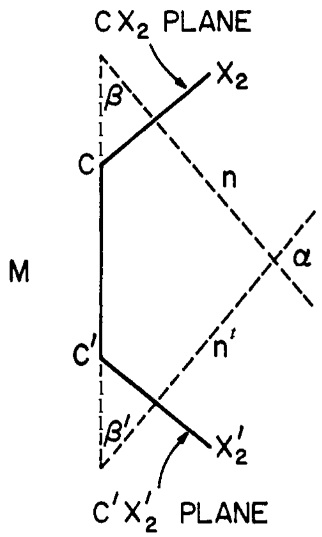

Figure 2. The definition of the angles α and β used to describe the nonplanarity of the $X_2C{-}C'X'_2$ ligand. The vectors *n* and *n'* are the normals to the CX_2 and $C'X'_2$ planes, respectively. Note that if the vectors *C–C'*, *n*, and *n'* are coplanar then $\alpha + \beta + \beta' = 180°$.

In Table VI the bond lengths in free tetracyanoethylene[20] are compared with those of this molecule coordinated in tetracyanoethylene oxide,[21] in the present compound, and in $IrBr(CO)(TCNE)(P(C_6H_5)_3)_2$.[1] (Insofar as we know, the only other molecule containing a similarly coordinated TCNE ligand for which structural details have been published is Pt(TCNE)(P-

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Table V. Distances (Å) and Angles (deg)

Bond Distances

Ni–C(1)	1.868 (5)	1.866 (5)[a]
Ni–C(3)	1.864 (5)	
Ni–C(5)	1.956 (4)	1.954 (4)
Ni–C(6)	1.951 (4)	
C(3)–N(2)	1.144 (5)	1.143 (5)
C(1)–N(1)	1.142 (5)	
N(1)–C(2)	1.462 (6)	1.463 (6)
N(2)–C(4)	1.464 (6)	
C(2)–C(11)	1.483 (8)	1.483 (18)
C(2)–C(12)	1.483 (8)	
C(2)–C(13)	1.456 (9)	
C(4)–C(14)	1.507 (8)	
C(4)–C(15)	1.498 (7)	
C(4)–C(16)	1.473 (8)	
C(5)–C(6)	1.476 (5)	
C(5)–C(9)	1.436 (6)	1.436 (6)
C(5)–C(10)	1.440 (6)	
C(6)–C(7)	1.431 (6)	
C(6)–C(8)	1.437 (6)	
C(7)–N(3)	1.132 (6)	1.142 (7)
C(8)–N(4)	1.148 (6)	
C(9)–N(5)	1.141 (6)	
C(10)–N(6)	1.145 (5)	

Nonbonded Distances

C(1)–C(5)	3.093 (6)
C(3)–C(6)	2.997 (6)
C(7)–C(9)	2.865 (7)
C(8)–C(10)	2.817 (7)
Ni–C(7)	2.854 (5)
Ni–C(8)	2.873 (5)
Ni–C(9)	2.902 (5)
Ni–C(10)	2.839 (5)
C(3)–C(7)	3.694 (7)
C(3)–C(8)	3.279 (7)
C(1)–C(9)	3.729 (7)
C(1)–C(10)	3.466 (6)

Bond Angles

C(1)–Ni–C(3)	98.9 (2)	
C(5)–Ni–C(6)	44.4 (2)	
C(1)–Ni–C(5)	108.0 (2)	
C(3)–Ni–C(6)	103.5 (2)	
Ni–C(1)–N(1)	176.9 (4)	
Ni–C(3)–N(2)	172.4 (4)	
C(1)–N(1)–C(2)	176.6 (4)	
C(3)–N(2)–C(4)	171.5 (4)	
N(1)–C(2)–C(11)	108.6 (4)	107.9 (10)
N(1)–C(2)–C(12)	108.2 (4)	
N(1)–C(2)–C(13)	106.8 (5)	
N(2)–C(4)–C(14)	106.6 (4)	
N(2)–C(4)–C(15)	109.1 (4)	
N(2)–C(3)–C(16)	108.1 (4)	
C(11)–C(2)–C(12)	111.3 (6)	111.0 (7)
C(11)–C(2)–C(13)	111.5 (6)	
C(12)–C(2)–C[13)	110.2 (6)	
C(14)–C(4)–C(15)	111.0 (5)	
C(14)–C(4)–C(16)	110.1 (6)	
C(15)–C(4)–C(16)	111.7 (5)	
Ni–C(5)–C(9)	116.8 (3)	
Ni–C(5)–C(10)	112.5 (3)	
Ni–C(6)–C(7)	114.2 (3)	
Ni–C(6)–C(8)	115.1 (3)	
C(7)–C(6)–C(8)	114.0 (4)	114.7 (6)
C(9)–C(5)–C(10)	115.3 (4)	
C(5)–C(6)–C(7)	119.0 (4)	118.4 (8)
C(5)–C(6)–C(8)	118.4 (4)	
C(6)–C(5)–C(9)	118.9 (4)	
C(6)–C(5)–C(10)	117.1 (3)	
C(5)–C(9)–N(5)	179.7 (5)	178.7 (11)
C(5)–C(10)–N(6)	177.3 (4)	
C(6)–C(7)–N(3)	178.4 (6)	
C(6)–C(8)–N(4)	179.4 (5)	

Vector–Plane Normal Angles[c]

C(5)–C(6) C(5)–C(10)–C(9)	61.3 (5)	61.6 (5)
C(6)–C(5) C(6)–C(7)–C(8)	61.9 (5)	
C(5)–C(6) Ni–C(1)–C(3)	82.2 (2)	

Dihedral Angles[b]

C(6)–C(7)–C(8) C(5)–C(10)–C(9)	56.8 (5)
Ni–C(5)–C(6) Ni–C(3)–C(1)	23.9 (2)
Ni–C(5)–C(6) C(5)–C(6)–C(7)	106.4 (4)
Ni–C(5)–C(6) C(5)–C(6)–C(8)	107.6 (4)
Ni–C(5)–C(6) C(6)–C(9)–C(5)	109.2 (4)
Ni–C(5)–C(6) C(6)–C(10)–C(5)	104.7 (3)

[a] These are average quantities. 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. [b] 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) × V(2). Form a similar normal to the plane of B(1)–B(2)–B(3). Then the dihedral angle is defined as the angle between these two normals. [c] 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).

$(C_6H_5)_3)_2$. However, the preliminary report[22] does not provide the necessary data for the present comparison.) The data of Table VI suggest that the effects of coordination on the C_α–C_β and C_β–N bond lengths are scarcely discernible, but that there is the expected effect on the central C_α–C_α bond. Such a lengthening is expected on the basis of the usual descriptions of the π bonding of olefins to transition metals,[23,24] where

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Table VI. Geometry of Uncoordinated and Coordinated Tetracyanoethylene

Compound	$\langle C_\alpha–C_\alpha\rangle$[a]	$\langle C_\alpha–C_\beta\rangle$	$\langle C_\beta–N\rangle$
TCNE[b]	1.339 (8)	1.441 (5)	1.134 (6)
$IrBr(CO)(TCNE)(P(C_6H_5)_3)_2$[c]	1.506 (15)	1.451 (6)	1.141 (12)
$Ni(TCNE)(t\text{-}BuNC)_2$[d]	1.476 (5)	1.436 (6)	1.142 (7)
TCNE oxide[e]	1.497 (4)	1.450 (4)	1.129 (4)

[a] The central carbon atoms are denoted C_α. The other carbon atoms are denoted C_β. [b] Reference 20. TCNE = tetracyanoethylene. [c] Reference 1. [d] Present work. [e] Reference 21.

Table VII. Geometry of Uncoordinated and Coordinated Olefins, $X_2C{=}CX_2$

Compound	$\alpha = \angle(CX_2/CX_2)$, deg[a]	$\beta = \angle(C–C/CX_2)$, deg[a]	C–C, Å
C_2H_4[b]	0	90	1.344 (10)
TCNE[c]	0	90	1.339 (8)
$K[PtCl_3(C_2H_4)]\cdot H_2O$	35[d,e]	72.5[e]	1.354 (15),[e] 1.44 (4)[f]
$Ni(TCNE)(t\text{-}BuNC)_2$[g]	56.8 (5)	61.6 (5)	1.476 (5)
$IrBr(CO)(TCNE)(P(C_6H_5)_3)_2$[h]	70.4 (13)[d]	54.8 (15)	1.506 (15)
TCNE oxide[i]	52.3	63.8	1.497 (4)

[a] These angles are defined in Table V and Figure 2. [b] B. P. Stoicheff, *Can. J. Phys.*, **33**, 811 (1955). [c] Reference 20. [d] The supplements of these angles were used in ref 1. [e] Reference 25. [f] Reference 26. [g] Present work. [h] Reference 1. [i] Reference 21.

there is back-donation from the metal orbitals into the π^* antibonding orbitals of the ligand. This description is not applicable to tetracyanoethylene oxide, where presumably the O–C bonds are largely σ in character.

In addition to changes in the central C–C bond length, simple alkene ligands $X_2C{=}CX_2$ become nonplanar on coordination to the metal. Figure 2 sketches some definitions of angles useful to describe this nonplanarity. Since these angles can only be determined if the positions of the X atoms can be located, there are only a very limited number of structural studies which bear on this nonplanarity and these results are collected together in Table VII. The striking feature of these results is that as the C–C bond lengthens the angle α increases and the CX_2 groups bend further away from the metal. In fact, from the results on the TCNE molecule and on transition metal compounds containing TCNE as a ligand, one finds the very simple expression $\delta\beta = 209\delta l$, where $\delta\beta$ is the change in degrees from 90° in the angle β defined in Figure 2 and δl is the change in ångströms in the central C–C bond length from 1.339 Å. This relationship predicts a C–C bond length of 1.43 Å in Zeise's salt, rather closer to the X-ray value[25] than to the neutron diffraction value.[26] The reason for the disagreement in these two determinations is not obvious, although there is now doubt about the correctness of the original space group assignment.[27]

Somewhat surprisingly, the degree of nonplanarity of the TCNE ligand in the present compound and in tetracyanoethylene oxide is very similar. Moreover, the central C–C bond distances are surprisingly close in view of the rather different factors involved in the bonding of TCNE to a transition metal as opposed to an oxygen atom.

If one accepts the π-bonding model of olefin attachment, then the greater the electron density available on the metal for back-donation to the olefin the longer the resultant C–C bond and the more stable the complex. Although the central C–C bond length of 1.476 (5) Å found in the present study is only marginally shorter than that of 1.52 (3) Å in $Pt(TCNE)(P(C_6H_5)_3)_2$,[22] this is the expected trend. Thus, on the basis of the effects of the metal on the O–O bond length in molecular oxygen complexes,[28] we expect Pt to be more electron rich than Ni. And in view of the stability of the $Ni(C_2H_4)(P(C_6H_5)_3)_2$ molecule, we believe that triphenylphosphine is a better electron donor than *t*-butyl isocyanide. But for a meaningful comparison to be made of the relative importance of change of metal and change of ligand structural details on $Pt(TCNE)(t\text{-}BuNC)_2$ or $Ni(TCNE)(P(C_6H_5)_3)_2$ are needed.

The distortion of the olefin on coordination to the metal atom mixes orbitals which were previously exclusively π or σ. If the coordination becomes strong enough and the resultant distortion great enough one might wish to speak of the central carbon atoms as being sp^3 hybrids. The angle α would then be 109° 28′. On the basis of the data of Table VII such a description does not appear to be warranted for the compounds discussed here. Previously[7] we have presented an argument, based on the central C–C bond distance rather than bond angles, which is also against the description of the central carbon atoms as being sp^3 hybridized.

Table VIII presents data on least-squares planes through various atoms in the present structure. The only groups which are strictly planar are the $C(CN)_2$ groups. In particular, the central C atoms of the TCNE ligand do not lie in the plane defined by the Ni and the two bonding C atoms of the *t*-BuNC groups. As indicated in Table V, the dihedral angle between the normal to the Ni–C (of TCNE) plane and the normal to the Ni–C (of *t*-BuNC) plane is 23.9 (2)°. The fact that the C–C vector is usually in the ML_2 plane in trigonal-bipyramidal complexes and is usually normal to the ML_3 plane in square-planar complexes can be rationalized qualitatively on the basis of minimization of nonbonded interactions,[1] although electronic effects[29] may also be important. Clearly there are no steric effects of any import in trigonal complexes, such as the present one. Thus it is important to examine the orientation of the olefin relative to the ML_2 plane. At face value, the present dihedral angle of 23.9° is the largest deviation from planarity of the $ML_2(C_2)$ portion of such trigonal molecules

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Table VIII. Weighted Least-Squares Planes

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

Plane no.	A, Å	B, Å	C, Å	D, Å
1	0.363	−10.073	1.980	−1.109
2	1.499	−10.053	−1.045	−1.681
3	2.244	−9.907	−2.462	−1.901
4	8.224	−1.744	−16.336	−4.332
5	0.831	1.828	16.954	5.337

Deviations from the Planes, Å

Atom	Plane No. 1	2	3	4	5
Ni	0.0172 (6)	0.0360 (6)	0.0392 (6)		
N(1)		−0.255 (4)	−0.191 (4)		
N(2)		−0.317 (4)	−0.067 (4)		
N(3)				0.007 (5)	
N(4)				−0.001 (6)	
N(5)					0.001 (5)
N(6)					0.005 (4)
C(1)	−0.310 (4)	−0.158 (4)	−0.120 (4)		
C(2)			−0.257 (6)		
C(3)	−0.355 (4)	−0.089 (4)	0.068 (4)		
C(4)			−0.447 (5)		
C(5)	−0.249 (4)	−0.545 (4)	−0.702 (4)		0.003 (4)
C(6)	−0.082 (4)	−0.311 (4)	−0.406 (4)	0.002 (4)	
C(7)				−0.010 (5)	
C(8)				0.002 (5)	
C(9)					−0.002 (5)
C(10)					−0.008 (4)

yet reported. Previously angles ranging from 6° in $Pt(FUMN)(P(C_6H_5)_3)_2$ (FUMN = fumaronitrile)[30] to 12° in $Ni(C_2H_4)(P(C_6H_5)_3)_2$[18] have been observed. (Data for a number of olefins are tabulated in ref 1.) Recently, Heimbach and Traunmüller[31] have put forward a qualitative scheme that attempts to account for such "twist angles" on the basis of electronic effects. Closer examination of the distortions in the present complex suggests that these are sufficiently complex to preclude the application of the ideas of Heimbach and Traunmüller. Thus, while it is true that the dihedral angle is 23.9° between the NiL_2 and NiC_2 planes, it also is true that the C–C vector makes an angle of 82.2 (2)° with the normal to the NiL_2 plane. On this basis there is not much of a "twist." Examination of least-squares plane no. 1 of Table VIII provides a better description of the distortions. The least-squares plane through the Ni and the four peripheral C atoms puts the Ni above the plane and all four carbon atoms below it. Thus the distortions not only involve a small twist but also a tendency toward a tetragonal pyramidal geometry. Although such distortions could be partially electronic in nature, they could also arise from simple minimization of packing energy in the solid state.

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