the plane, this would increase the movement required of the metal atom in hemoglobin.[40] On the other hand, the trans influence of the bound carbon monoxide molecule would proportionally decrease the movement of the proximal histidine.

Acknowledgments. The authors would like to thank Drs. Richard Kirchner and Jean-Jacques Bonnet for their help during the initial stages of data collection. We are indebted to Professor K. N. Raymond and Dr. S. Goldberg for assistance with the calculations at

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Structure and Mechanism of Formation of a Novel π-Bonded Ketenimine Complex, Bis(*tert*-butyl isocyanide)(*N-tert*-butyldicyanoketenimine)nickel(0). Evidence for a Metal-Assisted Carbene Addition

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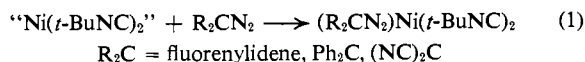**Yoshitaka Tatsuno,**[1b] **and Sei Otsuka**[1b]

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Abstract: A single-crystal X-ray study was carried out on the product of the reaction between Ni(*t*-BuNC)₄ and diazodicyanomethane, N₂C(CN)₂. The product is shown to be the ketenimine complex Ni(*t*-BuN=C=C(CN)₂)(*t*-BuNC)₂. Evidence is presented which shows that the reaction proceeds *via* an intermediate diazodicyanomethane complex, Ni(N₂C(CN)₂)(*t*-BuNC)₃. The remarkably facile thermal decomposition of this complex is proposed to involve a metal-assisted carbene addition to a coordinated isocyanide. The ketenimine complex thus formed crystallizes in space group D_{2h}^{15}-*Pbca* of the orthorhombic system, with eight molecules in a unit cell of dimensions $a = 10.199$ (3), $b = 34.283$ (9), and $c = 12.662$ (3) Å. The structure has been refined by least-squares techniques to a final R index of 4.1% based on 1905 reflections above background. The coordination about the Ni atom is approximately trigonal, if the ketenimine is regarded as a monodentate ligand. The ketenimine is coordinated to the metal *via* the carbon–heteroatom unsaturation. The cumulene system N=C=C is severely distorted from linearity upon coordination, the bond angle around the central carbon atom being 144.2 (4)°. A comparison is made between the structural parameters of the coordinated ketenimine and those of uncomplexed ketenimines.

There have been numerous reports[2–5] of the reactions of diazoalkanes with transition metal complexes. Generally such reactions have been shown to proceed with the extrusion of dinitrogen to form insertion products,[3] and recently some transition metal complexes containing the azine group (>C=N—N=C<) have been isolated.[4] It has been proposed[4] that the initial step in the formation of these azine complexes is a 1,3-dipolarophilic addition of the diazoalkane to generate

an intermediate four-membered ring complex. However, it is only recently that discrete transition metal complexes containing diazoalkane as a ligand have been reported.[5]

The reaction of "Ni(*t*-BuNC)₂"[6] with a variety of diazoalkanes leads to a series of Ni(0) complexes (eq 1). However, a different reaction occurs when

$$\text{``Ni}(t\text{-BuNC})_2\text{''} + R_2CN_2 \longrightarrow (R_2CN_2)Ni(t\text{-BuNC})_2 \quad (1)$$

$$R_2C = \text{fluorenylidene, Ph}_2C, (NC)_2C$$

Ni(*t*-BuNC)₄ is treated with the diazoalkane N₂C(CN)₂, and the product of this reaction was initially formulated[5] as the dimeric complex [Ni(*t*-BuNC)₃C(CN)₂]₂ from nmr and ir evidence. We now report the reformulation of this compound as the unexpected ketenimine complex Ni(*t*-BuN=C=C(CN)₂)(*t*-BuNC)₂ on the basis of a structural analysis and we then discuss the mechanism of formation.

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(5) S. Otsuka, A. Nakamura, T. Koyama, and Y. Tatsuno, *J. Chem. Soc., Chem. Commun.*, 1105 (1972).

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

Atom	Min	Inter	Max
Ni	0.216 (1)	0.229 (1)	0.311 (1)
C(1)	0.228 (5)	0.247 (5)	0.301 (6)
C(2)	0.220 (6)	0.267 (7)	0.314 (6)
C(3)	0.288 (6)	0.298 (7)	0.403 (7)
C(4)	0.228 (7)	0.321 (8)	0.570 (9)
C(5)	0.251 (7)	0.350 (7)	0.511 (9)
C(6)	0.209 (6)	0.242 (6)	0.323 (6)
C(7)	0.196 (6)	0.254 (6)	0.340 (6)
C(8)	0.255 (7)	0.357 (8)	0.441 (8)
C(9)	0.256 (7)	0.322 (6)	0.427 (7)
C(10)	0.234 (7)	0.314 (7)	0.562 (9)
C(11)	0.220 (6)	0.280 (6)	0.345 (6)
C(12)	0.256 (6)	0.282 (6)	0.321 (6)
C(13)	0.243 (6)	0.292 (7)	0.318 (6)
C(14)	0.221 (6)	0.245 (6)	0.270 (6)
C(15)	0.229 (5)	0.235 (6)	0.272 (6)
C(16)	0.213 (6)	0.256 (6)	0.316 (6)
C(17)	0.227 (6)	0.278 (6)	0.333 (6)
C(18)	0.205 (6)	0.282 (7)	0.377 (7)
N(1)	0.232 (5)	0.267 (4)	0.295 (5)
N(2)	0.220 (5)	0.236 (5)	0.342 (5)
N(3)	0.214 (5)	0.224 (4)	0.304 (5)
N(4)	0.243 (5)	0.337 (5)	0.422 (6)
N(5)	0.236 (6)	0.299 (6)	0.491 (7)
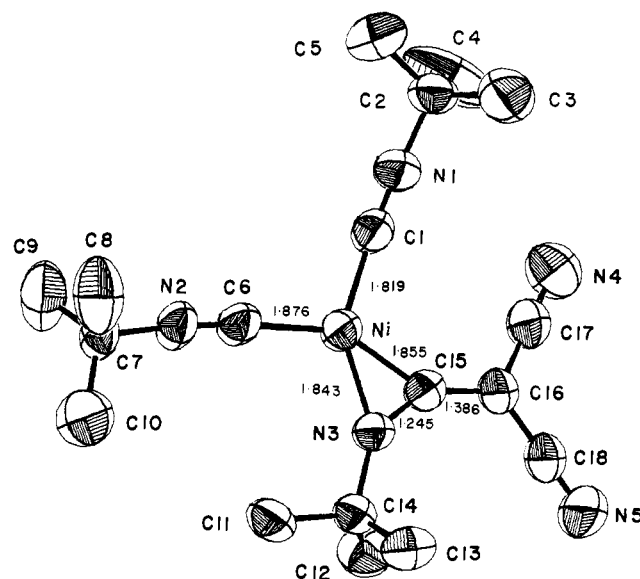
Figure 1. A drawing of the Ni[t-BuN=C=C(CN)$_2$](t-BuNC)$_2$ molecule. Hydrogen atoms have been omitted. The 50% probability vibrational ellipsoids are shown.

Table II. Positional and Thermal Parameters for Ni[t-BuN=C=C(CN)$_2$](t-BuNC)$_2$

Atom	x	y	z	$10^4\beta_{11}{}^a$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ni	0.19155 (7)^b	0.12884 (2)	0.23745 (5)	182 (1)	8.59 (7)	60.4 (5)	−3.3 (2)	4.3 (6)	1.1 (1)
C(1)	0.2728 (5)	0.1753 (1)	0.2137 (3)	172 (7)	10.0 (5)	66 (3)	−1 (2)	1 (4)	−1.7 (9)
C(2)	0.4076 (5)	0.2374 (1)	0.1650 (4)	144 (7)	8.5 (4)	113 (4)	−4 (1)	16 (4)	−2 (1)
C(3)	0.5162 (6)	0.2241 (1)	0.0967 (4)	229 (9)	14.1 (6)	160 (6)	−1 (2)	56 (6)	−2 (2)
C(4)	0.3220 (6)	0.2643 (2)	0.1067 (6)	195 (11)	14.7 (7)	355 (12)	−1 (2)	1 (8)	42 (2)
C(5)	0.4577 (7)	0.2557 (2)	0.2644 (5)	351 (13)	21.2 (9)	166 (7)	−39 (3)	52 (7)	−26 (2)
C(6)	0.1754 (5)	0.1250 (1)	0.3847 (3)	197 (7)	7.4 (4)	72 (4)	1 (1)	5 (4)	−1.1 (9)
C(7)	0.1443 (5)	0.1101 (1)	0.5842 (3)	217 (8)	10.5 (5)	52 (3)	2 (2)	10 (4)	4 (1)
C(8)	0.2781 (7)	0.1088 (2)	0.6339 (4)	276 (12)	29 (1)	88 (4)	16 (3)	12 (6)	11 (2)
C(9)	0.0656 (6)	0.1415 (2)	0.6351 (4)	290 (11)	19.9 (7)	99 (5)	18 (2)	53 (6)	3 (1)
C(10)	0.0818 (9)	0.0715 (2)	0.5889 (4)	562 (19)	18.4 (7)	78 (4)	−36 (3)	−1 (7)	8 (1)
C(11)	0.0401 (5)	0.0381 (1)	0.3004 (4)	191 (8)	12.3 (5)	88 (4)	−16 (2)	2 (4)	7 (1)
C(12)	0.0615 (5)	0.0467 (1)	0.1229 (4)	140 (7)	14.9 (6)	105 (4)	−5 (2)	−19 (4)	4 (1)
C(13)	0.1555 (5)	0.0144 (1)	0.1397 (4)	153 (8)	11.3 (5)	120 (4)	−5 (2)	−10 (4)	−4 (1)
C(14)	0.0658 (4)	0.0453 (1)	0.1841 (3)	131 (6)	9.1 (4)	72 (3)	−4 (1)	1 (4)	1.9 (9)
C(15)	0.1617 (4)	0.1078 (1)	0.1047 (3)	137 (6)	9.3 (4)	66 (3)	−3 (1)	−1 (3)	−1 (1)
C(16)	0.1670 (5)	0.1139 (1)	−0.0034 (3)	174 (7)	12.1 (5)	59 (3)	−9 (2)	5 (4)	2 (1)
C(17)	0.1943 (5)	0.1514 (1)	−0.0442 (3)	204 (8)	13.1 (6)	66 (3)	−5 (2)	4 (4)	3 (1)
C(18)	0.1441 (6)	0.0838 (2)	−0.0772 (3)	241 (9)	15.5 (6)	54 (3)	−16 (2)	7 (4)	3 (1)
N(1)	0.3296 (4)	0.2032 (1)	0.1939 (3)	162 (6)	9.3 (4)	88 (3)	−3 (1)	3 (3)	0.6 (9)
N(2)	0.1618 (4)	0.1201 (1)	0.4736 (3)	218 (7)	9.5 (4)	60 (3)	4 (1)	11 (3)	0.8 (8)
N(3)	0.1335 (4)	0.0835 (1)	0.1747 (2)	165 (5)	8.6 (3)	62 (2)	−8 (1)	−2 (3)	0 (1)
N(4)	0.2123 (5)	0.1816 (1)	−0.0790 (3)	332 (10)	14.8 (5)	108 (4)	−9 (2)	10 (5)	12 (1)
N(5)	0.1265 (6)	0.0589 (1)	−0.1367 (3)	405 (11)	19.5 (7)	69 (3)	−33 (2)	12 (5)	−3 (1)

^{a} The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^{b} Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant figures.

Discussion of the Structure of Ni(t-BuN=C=C(CN)$_2$)(t-BuNC)$_2$

Figure 1 presents a drawing of the Ni(t-BuN=C=C-(CN)$_2$)(t-BuNC)$_2$ molecule and indicates the numbering scheme. The vibrational thermal ellipsoids at their 50% probability level are also displayed in this figure and the root-mean-square amplitudes of vibration are presented in Table I. These vibrational data appear to be reasonable; as expected, the greatest thermal motion is shown by the methyl carbon atoms and the cyano nitrogen atoms. From the positional parameters in Table II and the correlation matrix, the relevant inter-atomic distances, bond angles, and their standard deviations were calculated and are presented in Table III.

The crystal structure consists of individual monomeric molecules, each of which is one asymmetric unit. The stereo drawing of eight complete molecules in a unit cell (Figure 2) represents a view along x. All inter-molecular contacts are normal, the shortest distance being 2.54 Å between C(13)H(2) and C(11)H(1) in adjacent molecules.

The Ni atom has its expected trigonal coordination where we consider the ketenimine molecule as a single ligand. The dihedral angle between the Ni–C(1)–C(6) and Ni–N(3)–C(15) planes is 7.9 (3)°, and the structure approximates more closely the essentially planar inner coordination sphere of the related bis($tert$-butyl isocyanide)(azobenzene)nickel(0)[7] (dihedral angle 1.2

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

Bond distances		Bond angles	
Ni–C(1)	1.819 (5)	C(1)–Ni–C(6)	105.4 (2)
Ni–C(6)	1.876 (4)	C(15)–Ni–N(3)	39.5 (1)
Ni–C(15)	1.855 (4)	C(1)–Ni–C(15)	105.4 (2)
Ni–N(3)	1.843 (3)	C(6)–Ni–N(3)	109.9 (2)
C(1)–N(1)	1.149 (5) } 1.148 (5)ᵃ	C(15)–Ni–C(6)	149.2 (2)
C(6)–N(2)	1.147 (5) }	C(1)–Ni–N(3)	144.4 (2)
N(1)–C(2)	1.464 (5) } 1.459 (8)	Ni–C(1)–N(1)	175.3 (4) } 175.3 (4)
N(2)–C(7)	1.453 (5) }	Ni–C(6)–N(2)	175.2 (4) }
C(2)–C(3)	1.477 (6)	C(1)–N(1)–C(2)	176.5 (4) } 175.6 (10)
C(2)–C(4)	1.469 (7)	C(6)–N(2)–C(7)	174.8 (4) }
C(2)–C(5)	1.496 (7) }	N(1)–C(2)–C(3)	107.8 (4) }
C(7)–C(8)	1.503 (8) } 1.484 (14)	N(1)–C(2)–C(4)	107.8 (4)
C(7)–C(9)	1.489 (6) }	N(1)–C(2)–C(5)	108.0 (4) }
C(7)–C(10)	1.470 (7) }	N(2)–C(7)–C(8)	107.4 (4) } 107.8 (4)
C(14)–C(11)	1.516 (6) }	N(2)–C(7)–C(9)	108.2 (4)
C(14)–C(12)	1.513 (6) } 1.512 (6)	N(2)–C(7)–C(10)	107.7 (4) }
C(14)–C(13)	1.508 (6) }	N(3)–C(14)–C(11)	107.6 (3) }
C(14)–N(3)	1.485 (5)	N(3)–C(14)–C(12)	109.2 (3) } 108.2 (3)
N(3)–C(15)	1.245 (4)	N(3)–C(14)–C(13)	107.9 (3) }
C(15)–C(16)	1.386 (5)	C(3)–C(2)–C(4)	110.2 (5)
C(16)–C(17)	1.413 (6) } 1.413 (6)	C(3)–C(2)–C(5)	111.5 (5) }
C(16)–C(18)	1.413 (6) }	C(4)–C(2)–C(5)	111.3 (5) }
C(17)–N(4)	1.139 (5) } 1.146 (10)	C(8)–C(7)–C(9)	109.2 (5) } 110.9 (15)
C(18)–N(5)	1.152 (5) }	C(8)–C(7)–C(10)	110.6 (5) }
		C(9)–C(7)–C(10)	113.5 (5) }
		C(11)–C(14)–C(12)	110.8 (4) }
		C(11)–C(14)–C(13)	110.6 (4) } 110.7 (4)
		C(12)–C(14)–C(13)	110.6 (4) }

Dihedral anglesᵇ			
Ni–N(3)–C(15) } Ni–C(6)–C(1) }	172.2 (3)	Ni–N(3)–C(14)	149.1 (3)
Ni–N(3)–C(15) } C(15)–C(16)–C(18) }	7.5 (5)	Ni–N(3)–C(15)	70.8 (2)
Ni–N(3)–C(15) } C(17)–C(16)–C(15) }	7.9 (3)	Ni–C(15)–N(3)	69.7 (2)
Ni–N(3)–C(15) } C(15)–N(3)–C(16) }	0.4 (8)	Ni–C(15)–C(16)	146.1 (3)
Ni–N(3)–C(15) } C(14)–N(3)–C(15) }	11.5 (6)	C(14)–N(3)–C(15)	138.7 (3)
Ni–N(3)–C(15) } N(2)–C(6)–Ni }	6 (3)	N(3)–C(15)–C(16)	144.2 (4)
Ni–N(3)–C(15) } Ni–C(1)–N(1) }	131 (5)	C(15)–C(16)–C(17)	120.4 (4) } 121.4 (14)
Ni–C(1)–N(1) } N(2)–C(6)–Ni }	134 (5)	C(15)–C(16)–C(18)	122.4 (4) }
C(16)–C(17)–C(18) } C(15)–N(3)–C(14) }	161.6 (5)	C(17)–C(16)–C(18)	117.2 (4)
		C(16)–C(17)–N(4)	177.6 (6) } 178.4 (11)
		C(16)–C(18)–N(5)	179.2 (6) }

Vector–plane normal anglesᵇ	
C(15)–N(3) } C(16)–C(17)–C(18) }	84.0 (5)
N(3)–C(15) } Ni–C(6)–C(1) }	97.5 (3)
N(3)–C(15) } C(15)–C(16)–C(18) }	85.8 (6)
N(3)–C(15) } C(15)–C(16)–C(17) }	94.6 (4)

ᵃ These are average quantities. The estimated standard deviation in the parentheses is the larger of an individual standard deviation or of the standard deviation of a single observation as calculated from the mean. ᵇ The senses of these angles are defined in ref 8.
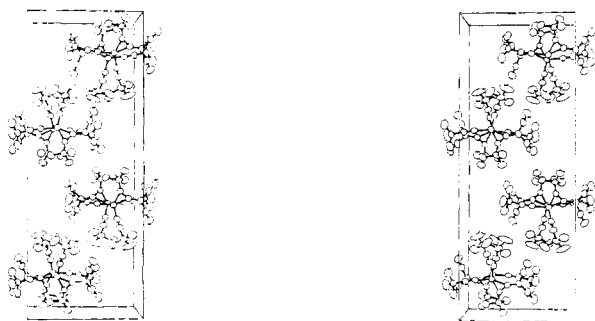

Figure 2. A stereoscopic drawing of eight molecules of Ni[t-BuN=C=C(CN)₂](t-BuNC)₂ whose central metal atoms all lie within the same unit cell.

(3)°) than the more distorted structure of bis(*tert*-butyl isocyanide)(tetracyanoethylene)nickel(0)⁸ (di-

hedral angle 23.9 (2)°). The reasons for the differences in dihedral angles between the structures are not obvious,⁹ but one set of calculations¹⁰ does indicate that a planar configuration should be most stable for an isolated zerovalent metal complex. Various weighted least-squares planes through the molecule are presented in Table IV. These planes also provide a measure of the nonplanarity.

The distances from the nickel atom to the α-carbon atoms of the *t*-BuNC groups are 1.876 (4) and 1.819 (5) Å, the shorter distance being associated with the *t*-BuNC group trans to the nitrogen atom of the keten-

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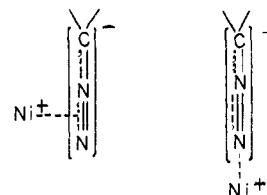
Table IV. Weighted Least-Squares Planes

Plane no.	Plane Equation: $Ax + By + Cz - D = 0$, with x, y, z in Orthorhombic Coordinates			
	A	B	C	D
1	8.897	−16.719	0.419	−0.353
2	9.257	−14.294	0.609	0.079
3	9.380	−13.454	−0.051	0.052
4	9.081	−15.413	−0.895	−0.255
5	9.980	−7.068	−0.036	0.854
6	9.965	−7.155	−0.515	0.864
7	9.869	−8.545	−0.480	0.669
8	9.663	−10.912	−0.385	0.343

Deviations from the Planes, Å
Plane no.

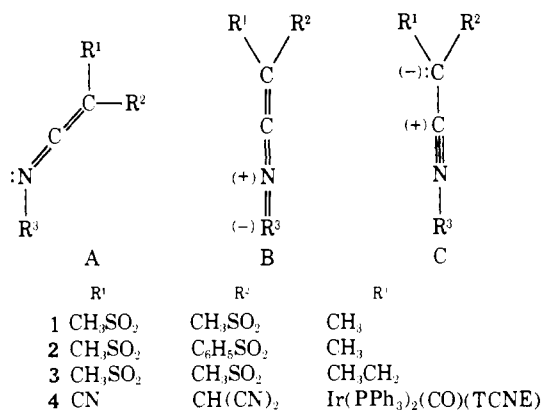|	1	2	3	4	5	6	7	8
Ni	0.0026 (7)	−0.0033 (7)	−0.0007 (7)			0.0010 (8)	0.0061 (8)	0.0110 (7)
C(1)	−0.060 (5)	0.071 (5)						
C(2)	0.079 (5)							
C(6)	−0.014 (4)	−0.007 (5)						
C(7)	0.041 (5)							
C(14)			−0.054 (4)	−0.011 (4)				−0.272 (4)
C(15)		−0.060 (4)	0.009 (4)	−0.032 (4)	−0.006 (4)	−0.078 (4)	−0.045 (4)	0.003 (4)
C(16)			−0.018 (5)	0.018 (5)	0.007 (5)	−0.013 (5)	0.006 (5)	0.029 (5)
C(17)					0.017 (5)	0.012 (5)	−0.024 (5)	−0.100 (5)
C(18)					−0.005 (6)	0.012 (6)	0.074 (6)	0.165 (6)
N(1)	−0.031 (3)							
N(2)	−0.016 (4)							
N(3)		0.069 (4)	0.067 (4)	0.023 (4)			−0.150 (4)	−0.032 (4)
N(4)					−0.016 (5)	−0.007 (5)	−0.088 (5)	−0.242 (5)
N(5)					−0.002 (6)	0.046 (6)	0.142 (6)	0.290 (6)
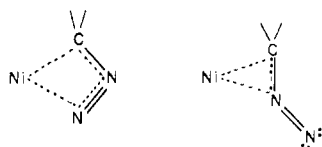
Figure 3. Proposed mode of coordination in Ni(N₂C(CN)₂)(t-BuNC)₂.

Figure 4. Proposed modes of coordination in Ni(N₂C(CN)₂)(t-BuNC)₃.

imine. These distances may be compared with the-average Ni–C (of t-BuNC) distances of 1.866 (5) Å for Ni(TCNE)(t-BuNC)₂[8] (TCNE = tetracyanoethylene) and 1.840 (5) Å for Ni(azobenzene)(t-BuNC)₂.[7] Relevant to the discussion is the observation that the two isocyanide, $\nu_{N\equiv C}$, bands at 2180 and 2160 cm⁻¹ occur at lower frequency than those bands in the analogous TCNE complex, yet higher than those found in other complexes of type NiL(t-BuNC)₂ (where L = azobenzene, fumaronitrile, dimethyl maleate).[11] This observation may be taken to imply that there is considerable back-bonding to the ketenimine ligand, and the electron affinity of this ligand may be inferred from the linear relationship of $\nu_{N\equiv C}$ with isostructural compounds NiL(t-BuNC)₂.[11]

The average C≡N and N—C distances in the C≡N—C fragment are 1.148 (5) and 1.459 (8) Å, respectively, and each fragment is essentially linear. The small deviations from linearity have been noted in similar structures[7,8] and perhaps result from packing forces. The average C–CH₃ distance for the tert-butyl group of the ketenimine is 1.512 (6) Å. A slightly shorter distance of 1.484 (14) Å is observed for the average C–CH₃ (of t-BuNC) bond lengths, but such shortening is probably apparent, rather than real, and is the result of vibrational effects.

(11) S. Otsuka, T. Yoshida, and Y. Tatsuno, *J. Amer. Chem. Soc.*, **93**, 6462 (1971).

Before discussing the mode of coordination of the ketenimine to the metal (Figures 3 and 4), it is necessary to review the nature of the ligand in the uncomplexed state. In the light of valence bond theory, the electronic structure of a ketenimine molecule may be regarded as being dependent upon relative contributions of the structures

	R¹	R²	R¹
1	CH₃SO₂	CH₃SO₂	CH₃
2	CH₃SO₂	C₆H₅SO₂	CH₃
3	CH₃SO₂	CH₃SO₂	CH₃CH₂
4	CN	CH(CN)₂	Ir(PPh₃)₂(CO)(TCNE)

N-Methyl-2,2-dimethylsulfonylketenimine[12] (1) and N-methyl-2-methylsulfonyl-2-phenylsulfonylketeni-

(12) P. J. Wheatley, *Acta Crystallogr.*, **7**, 68 (1954).

mine[13] (2) have been shown to possess an essentially linear skeleton and a short CN distance (1.154 and 1.148 Å for 1 and 2, respectively). The preponderance of contributions from structures of the type B and C in these molecules has been rationalized[12,13] on the basis of hyperconjugation involving the N-substituent introducing a contribution from B, and the action of the electronegative groups R^1 and R^2 inducing triple bond character into the NC bond (C). However, the observation[14] that N-ethyl-2,2-dimethylsulfonylketen-imine (3) possesses a bent skeleton (bond angle CNR^3 = 144.5°) and a slightly increased CN distance (1.165 Å) suggests an appreciable contribution from structure A. In all cases the CCN bond angle is approximately 180°.

In the present case, where N-tert-butyldicyanoketen-imine is coordinated to the metal via the carbon hetero-atom unsaturation, the observed NC bond length is 1.245 (4) Å. Thus, if molecules 1, 2, and 3 are accepted as suitable systems for comparison, then there is an appreciable lengthening of the NC bond upon coordina-tion, in accordance with the Chatt–Dewar–Duncanson model.[15] It is interesting to note that the σ-bonded keteniminato complex,[16] 4, possesses a short CN bond, 1.158 (11) Å, indicative of triple bond character.

The facility for back-bonding between the metal and ligand is demonstrated by the fact that the metal and the $NCC(CN)_2$ moiety are essentially coplanar (plane 7, Table IV). The activation of the unsaturated or-ganic ligand by the metal is further demonstrated by the deviation from colinearity of the bonds around the central carbon atom of the formal cumulene system. The bond angle, N(3)–C(15)–C(16), of 144.2 (4)° is of the same magnitude as the distortion that occurs around the central carbon atom of coordinated allenes.[17] In such complexes the metal is situated nearer the central carbon atom than a terminal carbon atom of the cumulene system. This result has been rationalized[17] by the assumption that the metal is involved in back-bonding with the two orthogonal π* orbitals at the central carbon atom. However, in the present case the Ni–N distance of 1.843 (3) Å is shorter than the Ni–C distance, 1.855 (4) Å, and this observation may be a reflection upon the electron distribution within the NC bond and the relative covalent radii of carbon and nitrogen atoms.

The bond length of the uncoordinated formal double bond, C(15)=C(16), is 1.386 (5) Å, and this distance is significantly greater than the analogous bond in the uncomplexed ketenimines, 1, 2, and 3 (bond distances 1.342, 1.354, and 1.356 Å, respectively). Such a varia-tion may only be a function of the different substituent groups at the terminal carbon atom, or it may be taken to indicate that in addition to back-bonding from a filled metal d orbital to the π* orbital of the N(3)–C(15) bond, there is also overlap at C(15) between the orthog-onal π* orbital of the C(15)–C(16) bond and a metal d orbital of the required symmetry. This π donation may be facilitated by the decrease in energy of this π* orbital caused by the cyano substituent groups at C(16).

The tert-butyl group is bent away from the metal to make a C(14)–N(3)–C(15) bond angle of 138.7 (3) Å. However, it is not known whether such a deviation from colinearity of atoms around N(3) is inherent in the un-complexed ketenimine (cf. 3) or is caused solely by activation of the ligand by the metal.

The features of this complex may be compared with those of another known π-bonded ketenimine com-plex $(MeN=C=CPh_2)Fe_2(CO)_6$.[18] The NCC bond angle in this compound is 127.5°, and the NC and CC bond distances are 1.36 and 1.38 Å. Such an elonga-tion of the NC bond length is not surprising, as in this binuclear iron complex the ketenimine is coordinated via a trihapto-NCC fragment, analogous to an allyl system.

Discussion of the Mechanism of Formation of $Ni(t\text{-}BuN=C=C(CN)_2)(t\text{-}BuNC)_2$

The result of the structural analysis, demonstrating that the product of the reaction between $Ni(t\text{-}BuNC)_4$ and $N_2C(CN)_2$ is a ketenimine complex and not the dimeric species $[Ni(t\text{-}BuNC)_3C(CN)_2]_2$ originally for-mulated,[5] instigated an examination of the mechanism of formation. The reaction paths which lead to the formation of the ketenimine complex, 7, are illustrated in Scheme I. Treatment of the tetrakisisocyanide

Scheme I
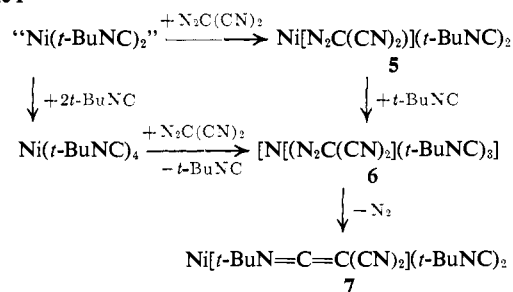
complex, $Ni(t\text{-}BuNC)_4$, with $N_2C(CN)_2$ in ether at −78° produced a suspension of the purple complex 6. On raising the temperature of the reaction mixture to −10°, dinitrogen was evolved, and the suspension changed into a beige solution from which yellow crystals of 7 were isolated in 57% yield. Complex 7 was also prepared by raising the temperature of a dilute toluene solution of 6 (prepared by dissolving the isolated 6 below −70°) to −10°. Under these conditions dinitrogen was evolved and 7 was isolated in quantitative yield.

Formation of complex 7 in high yield (88%) was also effected by the addition of ca. 2 mol of t-BuNC to the diazodicyanomethane complex 5, in toluene solu-tion at −78°. Dinitrogen was evolved on warming the reaction mixture to −10°, and the incipient formation of 6 during the course of the reaction was deduced from the color of the reaction mixture. Significantly, 6 was isolated in 55% yield by the addition of 1 mol of t-BuNC to 5 in toluene at −78°.

Complex 6 could not be characterized fully as its inherent thermal instability precluded satisfactory ele-mental analysis and molecular weight measurement. The formulation of this complex as $Ni[N_2C(CN)_2](t\text{-}BuNC)_3$ is proposed on the basis of the following ob-

(13) R. K. Bullough and P. J. Wheatley, Acta Crystallogr., 10, 233 (1957).

(14) J. J. Daly, J. Chem. Soc., 2801 (1961).

(15) J. Chatt and L. A. Duncanson, J. Chem. Soc., 2939 (1953); M. J. S. Dewar, Bull. Soc. Chim. Fr., 18C, 79 (1951).

(16) J. S. Ricci and J. A. Ibers, J. Amer. Chem. Soc., 93, 2391 (1971).

(17) T. G. Hewitt and J. J. De Boer, J. Chem. Soc. A, 817 (1971).

(18) K. Ogawa, A. Torii, H. Kobayashi-Tamura, T. Watanabé, T. Yoshida and S. Otsuka, Chem. Commun., 991 (1971).

servations. Dinitrogen was not evolved during formation from either **5** and 1 mol of t-BuNC or Ni(t-BuNC)$_4$ and N$_2$C(CN)$_2$. In addition, **6** was converted quantitatively to the ketenimine complex **7** with evolution of dinitrogen, but with no liberation of free t-BuNC (*vide infra*). A comparison of the ir active N≡C stretching frequencies of the t-BuNC ligands in **5** and **6** (Table V)

Table V. Infrared Spectra[a]

Compounds	$\nu_{N\equiv C}$[b]	$\nu_{C=N}$[c]	$\nu_{C=N=N}$[d]	$\nu_{N=C=C}$
5	2200, 2180	2210 sh	1550	
6	2165, 2150	2180 sh	1640[e]	
7	2180, 2160	2200, 2190		1710

[a] Measured in Nujol mull at *ca.* 25° unless otherwise stated. [b] The frequency of free t-BuNC (neat) is 2130 cm^{-1}. [c] The frequency of free diazodicyanomethane is 2225 cm^{-1}. [d] The frequency of free diazodicyanomethane is 2140 cm^{-1}. [e] Measured in Nujol mull at −15°. On raising the temperature, the band at 1640 cm^{-1} disappears and the band at 1710 cm^{-1} appears.

reveals that the decrease in frequency from **5** to **6** is comparable with the values (9–18 cm^{-1}) observed[11] for NiL(t-BuNC)$_2$ and NiL(t-BuNC)$_3$ (L = TCNE, fumaronitrile, maleic anhydride). Furthermore, the observation of a sharp singlet resonance in the nmr spectrum (Table VI) is consistent[11] with the spectra of

Table VI. Nmr Spectra for *tert*-Butyl Protons[a]

Compounds	τ, ppm (rel intensity)	
5	8.46 s[b]	
6	8.42 s[c]	
7	8.68 s (3 H)	8.90 s (6 H)[d]
	8.43 s (6 H)	8.63 s (3 H)[e]

[a] The *tert*-butyl protons of free t-BuNC give a triplet at 8.94, 8.95, 8.97 in toluene-d_8, or 8.55, 8.575, 8.60 in acetone-d_6. [b] Measured in acetone-d_6 at −38°, using TMS internal reference. [c] Measured in acetone-d_6 at −80°. [d] Measured in toluene-d_8 at 22°. [e] Measured in acetone-d_6 at 22.5°.

complexes of the type NiL(t-BuNC)$_3$. Acceptance of this proposed stoichiometry precludes a polymeric structure, as in general the maximum coordination number of zerovalent nickel complexes is four.

The molecular structure of complexes **5** and **6** cannot be deduced unambiguously from the available spectral data. The isocyanide groups of **5** exhibit two N≡C stretching bands in the same region of the ir spectrum as those of complexes of the type NiL(t-BuNC)$_2$[11] (*vide supra*), and on this basis a side-on π-type coordination of the diazoalkane functional group is suggested. This proposition is consistent with the observation that the NNC stretching frequency (2140 cm^{-1})[19] of free diazodicyanomethane decreases considerably upon coordination, implying electron drainage into the functional group from the metal. The structure illustrated in Figure 3 is consistent with the spectral data, although an exact description of the bonding scheme must await the results of a structural analysis now in progress.

A similar description of the structure of complex **6** is contrary to spectral observations. The increase in

(19) E. Ciganek, *J. Org. Chem.*, **30**, 4198 (1965).

the number of coordinating t-BuNC ligands from two in **5** to three in **6** would be expected[11] to cause an increase in the electron density on the metal available for back-bonding with the ligand. However, the N≡C and NNC stretching frequencies of **6** require a molecular structure in which back-bonding from the metal is less effective compared with the structure of **5**. A polymeric structure being excluded, the poor solubility of **6** in nonpolar solvents may be taken as an indication that a degree of ionicity is involved in the bonding of the NNC moiety to the metal. The bonding schemes depicted in Figure 4, involving σ-type electron donor-acceptor interactions, are possible structures for this complex. Such a variation in the mode of diazoalkane coordination in complexes **5** and **6** more readily explains the remarkably facile thermal decomposition of **6**.

The thermal decomposition of **6** was monitored at −15° by ir spectroscopy. The absorption at 1640 cm^{-1} gradually decreased in intensity, and a new absorption appeared at 1710 cm^{-1}, assignable to the NNC stretching frequency of the coordinated ketenimine. The reaction was complete within 20 min, and the fact that no absorption was detected at 2130 cm^{-1} was taken to indicate that dissociation of t-BuNC from complex **6** does not occur.

The ketenimine complex so formed exhibits two ir N≡C stretching frequencies whose values fall within a range of those observed[11] for NiL(t-BuNC)$_2$ (L = TCNE, azobenzene, fumaronitrile) and indicates effective π-back-bonding to the ketenimine ligand. The nmr spectrum of this complex exhibits a single singlet resonance for the *tert*-butyl protons of the t-BuNC ligands, and in this sense resembles the spectrum of analogous olefin complexes.[11] However, the structural analysis of **7** reveals an essentially planar inner coordination sphere, implying asymmetric t-BuNC ligands, and this suggests that the observed equivalence of the *tert*-butyl proton resonances in solution may arise from the relief of crystal packing forces allowing the molecule to assume a tetrahedral geometry. Alternatively the observed equivalence may arise from either intramolecular rotation of the ketenimine ligand or rapid exchange of t-BuNC through a dissociative mechanism.

In order to determine the role of the metal in assisting the formation of the ketenimine, a control reaction was conducted between t-BuNC and N$_2$C(CN)$_2$ in the absence of the transition metal complex. Under comparable conditions to those employed in the formation of **7**, a novel cycloadduct, **8**, was generated

8
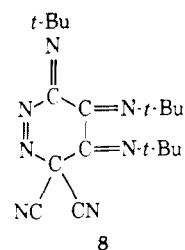
and no ketenimine was detected. This result is not surprising, although it has been reported[20] that a methoxycarbonylcarbene, derived from methyl phenyl-

(20) E. Ciganek, *J. Org. Chem.*, **35**, 862 (1970).

diazoacetate, reacts with isocyanide according to eq 2

$$R^1R^2CN_2 + CNR^3 \longrightarrow R^1R^2C=C=NR^3 \qquad (2)$$

(here R^1 = Ph, R^2 = COOCH$_3$). This apparent anomaly may be clarified by examining the electronic states of the reacting carbenes. Data on the reactions of methoxycarbonylcarbenes suggest that the ground state is a singlet.[21] However, the carbene generated by thermolysis of diazodicyanomethane is unable to undergo stereospecific cyclopropanation reactions, and this result[22] may be taken to indicate that the ground state of this carbene is a triplet.

Esr studies[23] have indicated that the ground electronic state of diphenylcarbene is triplet. In agreement with the spin conservation rule, this carbene does not react thermally with isocyanide to form a ketenimine but instead yields a ketazine as the major product (eq 3).

$$2Ph_2CN_2 \xrightarrow{-N_2} Ph_2C=NN=CPh_2 \qquad (3)$$
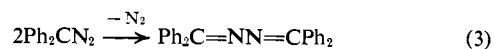
The photochemical reaction[24,25] of diphenyldiazomethane with alkyl isocyanide generates a ketenimine according to eq 2 and is understandable in terms of a singlet carbene reaction.

Hence the important conclusion may be reached that, through coordination to zerovalent nickel, diazodiacyanomethane is able to act as a singlet carbene source. Thus it has been demonstrated that the metal is able to control the electronic state of the reacting carbene. This result has far-reaching consequences in the design of carbene complexes for use in organic syntheses.

Experimental Section

Preliminary X-Ray Examination. The crystal selected for data collection was a square rod of approximate dimensions 0.2 × 0.2 × 1.1 mm and was mounted in a capillary. Preliminary precession photographs using Cu Kα radiation showed Laue symmetry *mmm*, and systematic absences were observed for 0*kl* for *k* odd, *h0l* for *l* odd, and *hk0* for *h* odd. These extinctions are characteristics of the orthorhombic space group D_{2h}^{15}-*Pbca*.

The crystal was transferred to a FACS-1 automatic diffractometer, and lattice parameters were obtained as previously described[26] by hand centering of 13 reflections with Cu Kα radiation (λ 1.540562 Å) in the range 30° ≤ 2θ ≤ 59°. The cell constants at 22° are *a* = 10.199 (3), *b* = 34.283 (9), and *c* = 12.662 (3) Å. A density of 1.12 g cm^{-3} calculated for eight formula units of Ni(*t*-BuNCC(CN)$_2$)(*t*-BuNC)$_2$ per unit cell agrees satisfactorily with that of 1.15 (2) g cm^{-3} measured by flotation of the material in hexane–CCl$_4$.

Collection and Reduction of Intensity Data. Data were collected on a Picker FACS-1 computer controlled four-circle diffractometer in a manner previously described.[27] A total of 3548 reflections were measured out to a 2θ (Cu Kα) value of 112° and these yielded 3309 unique reflections of which 1905 obeyed the condition $F_o^2 > 3\sigma(F_o)^2$, and these reflections were used in subsequent refinement. Six standard reflections from diverse parts of reciprocal space were measured after every 100 reflections, and the intensities of these reflections remained constant within counting statistics.

The data were collected by the θ–2θ scan technique using Cu Kα radiation prefiltered with Ni foil. The scan range in 2θ was from

−1.0° from the Kα$_1$ peak to +1.0° from the Kα$_2$ peak. The take-off angle was 2.9° and the receiving counter was positioned 32 cm from the crystal with an aperture 4.5 mm high and 5.0 mm wide. The pulse height analyzer was adjusted to admit approximately 85% of the Cu Kα peak. A scan rate of 2° in 2θ/min was used.

Initially background counts of 10 sec were taken at the end of each scan range, and this was increased to a count of 20 sec for reflections with 2θ values greater than 40°. Attenuators were automatically inserted if the intensity of the diffracted beam exceeded approximately 7000 counts per second during a scan. The attenuators were of Ni foil and gave attenuator factors of about 2.3. The data were processed in the manner previously described[26,27] to yield values of F_o^2 and $\sigma(F_o^2)$. A value of 0.04 for *p* was used in the estimation of standard deviations. Sample calculations[28] for an absorption correction were made using a linear absorption coefficient of 12.7 cm^{-1}. The transmission factors calculated were within the narrow range 0.79–0.80, and on this basis it was deemed unnecessary to apply an absorption correction.

Solution and Refinement of Structure. An unsharpened, three-dimensional Patterson function was computed. Harker vectors corresponding to the highest peaks in the map were consistent with four possible solutions for the position of the Ni atom, owing to the location of the atom upon a glide plane. By trial and error the correct solution was found, and refinement of the structure was continued using full-matrix least-squares techniques. Throughout the refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and where the weight, *w*, is $4F_o^2/\sigma^2(F_o^2)$. The agreement indices R_1 and R_2 are defined as $R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. The atomic scattering factors for all nonhydrogen atoms were taken from the usual tabulation,[29] while those for H were from the calculations of Stewart, *et al.*[30] The effects of anomalous dispersion were included in F_c.[31] The initial isotropic refinement converged to values of R_1 and R_2 of 0.146 and 0.191. After two cycles of anisotropic refinement, the hydrogen atom positions around the nine methyl groups were located from a difference Fourier synthesis. These positions were idealized (d(C–H) = 1.00 Å, H–C–H = 109.5°). Each hydrogen atom was assigned an isotropic temperature factor 1 Å^2 larger than that of the carbon atom to which it is attached. These positions are tabulated in Table VII. In subsequent structure factor calculations the contributions of these hydrogen atoms were taken into account. Two further cycles of anistropic refinement for 217 variables and 1906 observations reduced the values of R_1 and R_2 to 0.041 and 0.056, respectively, and led to the final parameters given in Table II.

An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices indicated no unusual trends and provided no evidence for extinction effects. The error in an observation of unit weight is 1.85 e. The maximum density on a final difference Fourier map is 0.17 e/Å^3, approximately 4% of the height of a carbon atom in this structure. The final values of the structure amplitudes are tabulated as $10|F_o|$ and $10|F_c|$ (in electrons) for those reflections used in the refinement.[32]

Preparations. ^{1}H nmr spectra were measured on a 100-MHz Model JNM 4H-100 instrument from Japan Electron Optics Laboratories, using TMS as internal reference. Ir spectra (Nujol mull) were recorded on a Hitachi-Perkin-Elmer Model 225. Ni(*t*-BuNC)$_4$,[6] "Ni(*t*-BuNC)$_2$,"[6] and diazodicyanomethane[19] were prepared by known methods. All reactions and physical measurements were carried out in a nitrogen atmosphere.

Preparation of Ni[N$_2$C(CN)$_2$](*t*-BuNC)$_2$ (5). To a suspension of "Ni(*t*-BuNC)$_2$" (0.219 g, 0.97 mmol) in ether (25 ml) was added slowly an ether solution (25 ml) of diazodicyanomethane (0.09 g,

(21) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).

(22) (a) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 1979 (1966). (b) Extended Hückel theory predicted the triplet state for the ground state of dicyanocarbene: R. Hoffmann, G. D. Zeiss, and G. W. Von Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).

(23) R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, **84**, 3213 (1962); R. W. Brandon, G. L. Closs, and C. A. Hutchinson, Jr., *J. Chem. Phys.*, **37**, 1878 (1962).

(24) J. A. Green and L. A. Singer, *Tetrahedron Lett.*, 5093 (1969).

(25) J. H. Boyer and W. Beverung, *Chem. Commun.*, 1377 (1969).

(26) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(27) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(28) In addition to various local programs for the CDC 6400, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program, the AGNOST absorption program, Johnson's ORTEP II thermal ellipsoid plotting program, Busing's and Levy's ORFFE error function program. Our least-squares program, NUCLS, in its nongroup form, closely resembles the Busing and Levy ORFLS program. Final calculations were carried out by remote hook-up with the CDC 7600 at Lawrence Berkeley Laboratories. Programs used were very minor modifications of the above.

(29) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography," Vol. 4, Kynoch Press, Birmingham, England, Table 2.2A, in press.

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

(31) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **18**, 17 (1965).

(32) See paragraph at end of paper regarding supplementary material.

Table VII. Calculated Hydrogen Positional Parameters

Atom	x	y	z
C(3)H(1)	0.563	0.201	0.129
C(3)H(2)	0.479	0.215	0.025
C(3)H(3)	0.579	0.245	0.082
C(4)H(1)	0.271	0.282	0.154
C(4)H(2)	0.365	0.279	0.049
C(4)H(3)	0.246	0.248	0.067
C(5)H(1)	0.508	0.234	0.310
C(5)H(2)	0.525	0.276	0.251
C(5)H(3)	0.388	0.265	0.310
C(8)H(1)	0.334	0.086	0.605
C(8)H(2)	0.276	0.105	0.714
C(8)H(3)	0.331	0.133	0.620
C(9)H(1)	0.093	0.167	0.611
C(9)H(2)	0.074	0.140	0.715
C(9)H(3)	−0.032	0.138	0.619
C(10)H(1)	−0.008	0.072	0.564
C(10)H(2)	0.088	0.060	0.662
C(10)H(3)	0.135	0.053	0.540
C(11)H(1)	−0.008	0.013	0.313
C(11)H(2)	0.124	0.038	0.342
C(11)H(3)	−0.017	0.060	0.330
C(12)H(1)	−0.119	0.068	0.150
C(12)H(2)	−0.044	0.050	0.046
C(12)H(3)	−0.111	0.021	0.131
C(13)H(1)	0.165	0.018	0.061
C(13)H(2)	0.244	0.017	0.173
C(13)H(3)	0.119	−0.012	0.152

0.97 mmol) at −78° under stirring. After stirring for 2–3 hr at −78 to −50°, the red suspension turned into a pale brown suspension. The air-sensitive pale brown precipitates were filtered, washed with n-hexane at −78°, and dried in $vacuo$, to give the analytically pure sample almost quantitatively. The complex is very soluble in acetone, slightly soluble in ether and toluene, and insoluble in n-hexane. The solution readily deteriorates at 0°. Recrystallization from toluene–n-hexane at −20° gave pale brown silky crystals, 85° dec. $Anal.$ Calcd for $C_{13}H_{18}N_6Ni$: C, 49.25; H, 5.72; N, 26.51. Found: C, 49.28; H, 5.80; N, 26.41.

Preparation of Ni[t-BuN=C=C(CN)$_2$](t-BuNC)$_2$ (7). To a suspension of Ni(t-BuNC)$_4$ (0.501 g, 1.28 mmol) in a mixture of ether (20 ml) and n-hexane (20 ml) was added slowly a solution of diazodicyanomethane (0.14 g, 0.52 mmol) in ether (20 ml) at −78° under stirring. The initially yellow suspension instantly turned into a purple suspension without evolution of dinitrogen. The temperature was allowed to rise to −10°, dinitrogen evolved quantitatively (32 ml, $ca.$ 1.3 mmol), and the suspension turned into a beige solution containing a black insoluble, untractable, tarry material. The beige solution was concentrated in $vacuo$ to give a yellow solid. Recrystallization from a mixture of ether and n-hexane gave yellow prisms (0.272 g, 57.3%), mp 173–175° dec. The complex is moderately stable in air and soluble in common organic solvents except the paraffins, such as n-hexane. The preparative reaction carried out at 0° gave the same product in lower yields. $Anal.$ Calcd for $C_{18}H_{27}N_5Ni$: C, 58.09; H, 7.31; N, 18.82. Found: C, 58.01; H, 7.49; N, 18.60.

Isolation of "Ni[N$_2$C(CN)$_2$](t-BuNC)$_3$" (6). To a suspension of Ni(t-BuNC)$_4$ (0.254 g, 0.683 mmol) in a mixture of ether (20 ml) and n-hexane (20 ml), was added an ether solution (20 ml) of diazodicyanomethane (0.064 g, 0.695 mmol) at −78° under stirring. A purple precipitate appeared in a few minutes. The precipitate was filtered, washed with 10 ml of ether two times at −78°, and dried under high vacuum (10^{-3} mm) below −40°. The yield was almost quantitative. The complex 6 is extremely air-sensitive and thermally unstable decomposing even in the solid state above −6°. Thus an elemental analysis was impossible. The complex is soluble in acetone, slightly soluble in toluene, and insoluble in n-hexane and ether. A toluene solution of 6 was slowly warmed from −78° to 0° and the purple solution turned into a clear yellow solution from which 7 was obtained in quantitative yield as yellow crystals.

Reaction of Ni[N$_2$C(CN)$_2$](t-BuNC)$_2$, (5) with t-BuNC. On addition of t-BuNC (0.04 ml, 0.4 mmol) to a toluene suspension (30 ml) of 5 (0.118 g, 0.374 mmol) at −78°, the initial pale brown suspension turned instantly into a purple suspension. The reaction mixture was allowed to warm to ambient temperature and the suspension became a brown yellow solution which, upon treating with ether, afforded the yellow crystals, 7 (0.0760 g, 54.7%), and a brown powder (0.028 g). The brown powder could not be further purified. When ether was employed as the solvent for the reaction, the yield of 7 amounted to 67.6%. Similar treatment of 5 (0.071 g, 0.224 mmol) with an excess of t-BuNC (0.05 ml, 0.5 mmol) in toluene caused a color change indicative of the formation of 6 and afforded 7 (0.1964 g, 87.7%).

Reaction of Dicyanodiazomethane with t-BuNC. To a solution of t-BuNC (3 ml, 30 mmol) in ether (30 ml) was added an ether solution (30 ml) of diazodicyanomethane (0.1173 g, 1.274 mmol) at 0° under stirring. Evolution of dinitrogen was not observed up to 30°. An orange yellow solution was evaporated and extracted with n-hexane to give orange yellow crystals, 8 (0.310 g, 72.8%), mp 118–119° dec. The compound is air stable and inert to moisture. Its ir spectrum shows no characteristic bands of a ketenimine or amide group: mol wt (vapor pressure osmometry, benzene solution) calcd 341, found 324; ir (Nujol mull) ν_{max}(cm^{-1}) 2235 cm^{-1} (sharp, m, −C≡N), 2220 (sharp, m, −C≡N), 1740 (broad, m), 1713 (shoulder, m), 1580 (vs C=N−), 1460 (sharp, s), 1222 (broad, s, δC-(CH$_3$)$_3$), 1192 (broad, m, δC-(CH$_3$)$_3$), 1072 (sharp, s), 1020 (sharp, s), 980 (sharp, m), 895 (sharp, m); nmr (benzene-d_6, 22.5°, TMS) ppm 8.58 s (9 H), 8.62 (9 H), 8.70 (9 H). $Anal.$ Calcd for $C_{18}H_{27}N_7$: C, 63.32; H, 7.97; N, 28.71. Found: C, 63.47; H, 8.20; N, 28.24.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8590.