Cyclopropanation Reactions of Diazoalkanes with Substituted Olefins in the Presence and Absence of Nickel(0) and Palladium(0) Catalysts. The Structure of (Diazofluorene)bis(*tert*-butyl isocyanide)nickel(0); a Complex Containing a π-Bonded Diazofluorene Molecule

Akira Nakamura,[1a] Toshikatsu Yoshida,[1a] Martin Cowie,[1b] Sei Otsuka,*[1a] and James A. Ibers*[1b]

Contribution from the Departments of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan 560 and Northwestern University, Evanston, Illinois 60201. *Received July 21, 1976*

Abstract: Diazofluorene reacts with Ni(0) and Pd(0) complexes, $M(t\text{-}BuNC)_2$ or $M(PPh_3)_2(C_2H_4)$ (M = Ni or Pd), to give the corresponding diazofluorene complexes, ML_2(diazofluorene). The reduction in the C=N=N stretching frequency from 2055 cm^{-1} in free diazofluorene to ca. 1500 cm^{-1} in these complexes suggests a side-on, π-coordination of the diazofluorene ligand. Reaction of these diazofluorene complexes with substituted olefins (methyl acrylate or diethyl maleate) at 100 °C produces cyclopropanation products. In the absence of any Ni(0) or Pd(0) catalysts, diazofluorene reacts with the substituted olefins at 30 °C to produce 1-pyrazoline derivatives which slowly undergo ring contraction to form the corresponding cyclopropane derivatives. Diazomethane does not form a stable complex with Ni(0) or Pd(0) systems even at −78 °C. However, in the presence of Ni(0) or Pd(0) compounds, diazomethane readily reacts with substituted olefins to produce substituted cyclopropanes. In the absence of the metal compounds, diazomethane and substituted olefins produce 2-pyrazoline derivatives which do not undergo ring contraction to the corresponding cyclopropane derivatives, even in the presence of Ni(0) or Pd(0) catalysts. The structure of one diazofluorene complex, $Ni(t\text{-}BuNC)_2$(diazofluorene), has been confirmed by x-ray diffraction studies. The diazofluorene molecule is π-bonded to the Ni atom through the N-N multiple bond such that the N atoms are essentially equidistant from the Ni atom and the complete molecule, with the exception of the methyl groups of the *tert*-butyl ligands, is nearly planar. Some relevant metrical parameters are: Ni-N(diazofluorene), 1.874 (3) and 1.834 (3); Ni-C(t-BuNC), 1.844 (4) and 1.844 (5); N-N(diazofluorene), 1.245 (4); N-C(diazofluorene), 1.334 (4) Å; N-Ni-N(diazofluorene), 39.2 (1); N-N-C(diazofluorene), 133.8 (3)°. The compound crystallizes in the orthorhombic space group $D_{2h}{}^{15}$-*Pbca* in a cell of dimension a = 17.748 (3), b = 18.999 (4), c = 14.295 (2) Å, and Z = 8. Based on 3022 unique reflections, the structure was refined by full-matrix, least-squares techniques to agreement indices (on F^2) of $R = 0.076$ and $R_w = 0.129$. The conventional agreement index (on F) for the 2095 reflections having $F_o{}^2 > 3\sigma(F_o{}^2)$ is $R = 0.046$. An interesting correlation between the Ni-C distances, the $\nu_{C\equiv N}$ values, and the C-Ni-C angles of the t-BuNC ligands and the π acidity of the ligand, AB, in a series of complexes, $Ni(t\text{-}BuNC)_2(AB)$, is noted.

Within the rich field of transition metal carbene complexes the chemistry of nickel(0)-carbene complexes of the type $Ni(CR_2)L_n$ (n = 2, 3)[2] has remained to be explored. Unless stabilized by heteroatomic substituents attached to the carbenic carbon atom,[3] these nickel-carbene complexes apparently exist only as intermediates in such reactions as (1) the nickel(0) catalyzed valence isomerization of bicyclobutane,[4] (2) the nickel(0) catalyzed decomposition of diazoalkanes,[5] or (3) the stoichiometric, thermal decomposition of nickel(0)-diazoalkane complexes, $NiL_2(R_2CN_2)$.[5] In this regard the role of metal ions in the activation of diazoalkane molecules, leading to carbenoid reactions, has been the subject of much speculation.[6] Continuing our investigations of labile nickel(0)-diazoalkane complexes,[5] we have been able to isolate a diazofluorene complex, $Ni(t\text{-}BuNC)_2$(diazofluorene) (**1**), and have examined its thermal reactions with various olefins. We have also studied the related catalysis of nickel(0) complexes in olefin cyclopropanation reactions with diazoalkanes.

The bonding scheme of the diazoalkane molecule, a heterocumulene system, to low-valent, nickel triad metals has been discussed.[7,8] However, we felt that in order to elucidate unambiguously the bonding of the diazoalkane molecule in metal complexes a structural determination was required. We have therefore undertaken the structural characterization of complex **1** and report it here, together with the above chemistry. Owing to a drastic reduction in the C=N=N stretching frequency[5] from 2055 cm^{-1} in diazofluorene to 1509 cm^{-1} in complex **1**, it was felt that the diazofluorene molecule was not σ-bonded to the metal, as is usually observed in aryldiazo,[9-18] alkyldiazo,[19] and aryldiazene[20-25] complexes. Rather we suspected that the molecule is bonded in a side-on manner to the nickel atom. Similar so-called π-coordination has previously been observed for the azobenzene molecule in $Ni(t\text{-}BuNC)_2(PhN{=}NPh)$[26] and $Ni(PTol_3)_2(PhN{=}NPh)$,[27] and has been postulated for the diazofluorene and dicyanodiazomethane molecules in $MoCp_2$(diazofluorene)[28] and $Ni(t\text{-}BuNC)_2((NC)_2CN_2)$,[8] respectively. We were therefore interested in determining the factors which favor the π-coordination of these diazo molecules over the more usual σ-bonding mode. Furthermore, we thought that a knowledge of the bonding of the diazofluorene molecule in this complex would assist in understanding its reactions and the reactions of other diazoalkanes.

Experimental Section

Materials: (a) Metal Complexes. "$Ni(t\text{-}BuNC)_2$",[29] $Ni(PPh_3)_4$,[30] $NiI(PPh_3)_3$,[31] $NiCl_2(PPh_3)_2$,[32] $(Pd(t\text{-}BuNC)_2)_2$,[29] $PdBr_2(t\text{-}BuNC)_2$,[29] $Pd(PPh_3)_4$,[33] $PdBr_2(PPh_3)_2$,[34] and $M(PPh_3)_2$(diazofluorene) (M = Ni, Pd)[5] were prepared by literature methods.

(b) Organics. Diazofluorene,[35] diazomethane,[36] and ethyl diazoacetate[37] were prepared by standard methods. The following cyclopropane derivatives were prepared to identify the cyclopropanation products: methyl cyclopropanecarboxylate,[38] phenylcyclopropane,[39] n-hexylcyclopropane,[39] and norcarane.[39]

Reaction of Diazomethane with Olefins in the Presence of Various Nickel or Palladium Complexes. An ether solution (5 ml) of diazomethane (0.25 mol/L) was added to an ether solution of an olefin (1 mmol) and the catalyst (0.1 mmol) under pure dinitrogen at room temperature. The mixture was stirred at that temperature for 1.5 h, and was evaporated at reduced pressure. Volatile products were collected at −70 to −78 °C. GLC analysis of the volatile products revealed the presence of the cyclopropanation and C–H insertion products, $R\underline{CHCH_2CH_2}$ and $RCH{=}CHCH_3$, respectively. These products were identified by comparison with the GLC peaks of the authentic compounds. The results are shown in Table I.

Stoichiometric Reactions of Diazofluorene–Palladium Complexes, PdL_2(diazofluorene), with Dimethyl Maleate. (a) L = *t*-BuNC. The diazofluorene-palladium complex, Pd(*t*-BuNC)$_2$(diazofluorene), was prepared by mixing the equivalent quantities of Pd(*t*-BuNC)$_2$ (354 mg, 1.30 mmol) and diazofluorene (251 mg, 1.30 mmol) in ether (30 ml) at −78 to −60 °C. Chilled toluene (40 ml) was added to dissolve the yellow diazofluorene complex immediately after its preparation. Dimethyl maleate (3 ml, 20 mmol) was then added to the reaction mixture at −45 °C to give an orange solution. On raising the temperature over a 2-h period to 40 °C, the solution became almost black. Removal of the solvent and the unchanged olefin from the reaction mixture, by evaporation at reduced pressure, yielded a black viscous material which was extracted with hexane. The extracts were chromatographed on silica gel. The products were identified by comparing their IR spectra with those of authentic samples. The following compounds were obtained (yield based on chromatographed sample): 2,3-*trans*-dicarbomethoxyspiro(cyclopropane)-1,9-fluorene (3.8%), bisfluorenylideneazine (4.8%), *N-tert*-butylfluorenylideneketenimine (22.7%), and *n-tert*-butylfluorenylacetamide (9.1%).

(b) L = PPh_3. The bis(phosphine) complex, Pd(PPh$_3$)$_2$(diazofluorene), was prepared by the procedure described previously.[5] Dimethyl maleate and this bis(phosphine) complex (556 mg, 0.675 mmol) were mixed at −70 °C. This mixture was slowly warmed to room temperature over 2 h and then heated at 80 °C for 1 h. The almost black reaction mixture was concentrated at reduced pressure to give a black tarry residue, which was extracted with benzene and chromatographed on Florisil. The cyclopropanation product was obtained in 21% yield. The formation of bisfluorenylideneazine and bifluorenylidene was not detected.

Thermolysis of Ni(*t*-BuNC)$_2$(diazofluorene) in the Presence of Diethyl Maleate. Ni(*t*-BuNC)$_2$(diazofluorene) (0.31 g, 0.74 mmol) was dissolved in diethyl maleate (ca. 8 ml) at room temperature and the solution was then stirred and heated to 100 °C until the evolution of N_2 gas had ceased. The resulting dark brown solution was distilled at under 10 mmHg pressure at 95 °C to remove the excess diethyl maleate (identified by GLC). The residual, oily product was dissolved in benzene (5 ml), and *n*-hexane (15 ml) was added to give a dark red precipitate, which was identified as bisfluorenylideneazine (20 mg, 15%) by comparison of its IR spectrum and melting point with those of an authentic sample. The soluble part was separated by column chromatography (silica gel). Elution with *n*-hexane/benzene (5:1) gave *N-tert*-butylfluorenylideneketenimine (13 mg). Elution with *n*-hexane/benzene (4:1) gave a yellow solid. Recrystallization from *n*-hexane gave colorless needles (102 mg, 41%) which were identified by their IR and NMR spectra and mp (101 °C) as 2,3-*trans*-dicarboethoxyspiro(cyclopropane)-1,9-fluorene. Elution with *n*-hexane and benzene (3:1 ∼ 2:1) gave a colorless powder which was recrystallized from *n*-hexane (58 mg, 29%). It was identified by elemental analysis and IR and NMR spectra as *N-tert*-butylfluorenylacetamide, mp 200.0 ∼ 201.5 °C.

Thermolysis of Ni(*t*-BuNC)$_2$(diazofluorene) in the Presence of Ethyl Vinyl Ether. Ni(*t*-BuNC)$_2$(diazofluorene) (1.230 g 2.95 mmol) was dissolved in toluene (20 ml) and ethyl vinyl ether (20 ml). This solution was stirred at 60 ∼ 70 °C until the evolution of N_2 gas had ceased (3 h). Upon treating the resulting solution in the same way as in the reaction with diethyl maleate, a dark red oily product was obtained. It was separated by column chromatography. Elution with *n*-hexane/benzene (3:1 ∼ 1:1) gave bisfluorenylideneazine (90 mg, 17%), and elution with *n*-hexane/benzene (1:1) gave *N-tert*-butyl-9-fluorenecarboxamide (412 mg, 70%). Cyclopropane derivatives could not be obtained.

^{1}H NMR Investigation of the Interaction of Diethyl Maleate with Ni(*t*-BuNC)$_2$(diazofluorene). The observed ^{1}H NMR peak assigned to the olefinic protons of diethyl maleate appeared at δ 4.6 in the presence of Ni(*t*-BuNC)$_2$(diazofluorene) in C_6D_5 at ∼30 °C. The δ value is smaller than that observed (δ 5.6) for the olefin alone under the same conditions. The preformed diethyl maleate nickel(0) complex, Ni(*t*-BuNC)$_2$(EtO$_2$CCH=CHCO$_2$Et), exhibits the coordinated olefin proton signal at δ 3.4 in C_6D_6. When ethyl vinyl ether was used as the olefin no interaction was revealed by the ^{1}H NMR spectrum.

X-Ray Data Collection. Orange prisms of the complex, Ni(*t*-BuNC)$_2$(diazofluorene), suitable for x-ray diffraction studies, were obtained from an ether/*n*-hexane solution. The crystalline compound is unstable in air, so it was handled in an N_2 atmosphere and crystals were mounted in N_2-filled capillaries.

Table I. Catalyzed Carbenoid Reaction between Diazomethane and Methyl Acrylate[a]

Catalyst	—CO$_2$CH$_3$, %	$CH_3CH{=}CHCO_2$-CH_3, %
Ni(*t*-BuNC)$_2$	66.5	20.4
Ni(PPh$_3$)$_4$	72.0	7.1
Ni(PPh$_3$)$_3$I	41.5	11.3
Ni(PPh$_3$)$_2$Cl$_2$	2.3	0.7
Pd(*t*-BuNC)$_2$[b]	0.9	24.4
Pd(*t*·BuNC)$_2$Br$_2$	0.4	4.9
Pd(PPh$_3$)$_4$	1.3	0.2
Pd(PPh$_3$)$_2$Br$_2$	1.2	3.2

[a] In ether, with ca. 10 mol % catalyst under nitrogen for 1.5 h. [b] The reaction performed at −78 °C to room temperature

Preliminary film data showed that the crystals belong to the orthorhombic system with extinctions (0*kl*, $k = 2n + 1$; *h*0*l*, $l = 2n + 1$; *hk*0, $h = 2n + 1$) characteristic of the space group $D_{2h}{}^{15}$-*Pbca*. Accurate cell parameters were obtained from a least-squares refinement of the setting angles of 15 reflections which were centered on a Picker four-circle diffractometer using a narrow x-ray source. These reflections were chosen from diverse regions of reciprocal space with $50.6° \leq 2\theta \leq 58.8°$. See Table II for pertinent crystal information. The crystal mosaicity was found to be acceptable for the θ–2θ scan technique based on ω scans performed with an open counter. No experimental density was obtained owing to the extreme air sensitivity of the complex. However the calculated value (1.149 g/cm^3) is reasonable for eight molecules in the cell.

Data were collected on a Picker computer-controlled diffractometer equipped with a scintillation counter and a pulse height analyzer which was set to accept 90% of the Cu Kα peak. Background counts were measured at both ends of the scan range with the counter and crystal stationary. The intensities of six standard reflections were measured every 100 reflections to assess decomposition effects. No significant change in the standards was observed.

The intensities of 3418 reflections with $2\theta \leq 110°$ were measured using Ni-filtered Cu Kα X-radiation. Beyond this point very few reflections were observed. The data were processed in the usual way using a value of 0.04 for *p*.[40] Of the measured reflections 3022 are unique and 2095 have $F_o{}^2 > 3\sigma(F_o{}^2)$. An absorption correction was applied to the data using Gaussian integration.[41]

Solution and Refinement of Structure. The Ni atom was located in an origin removed, sharpened Patterson synthesis. Subsequent refinements and difference Fourier syntheses led to the location of all non-hydrogen atoms. The structure was refined by full-matrix, least-squares techniques. The quantity minimized was $\Sigma w(F_o{}^2 - F_c{}^2)^2$ with $w = 1/\sigma^2(F_o{}^2)$. The agreement indices for refinement on $F_o{}^2$ are $R = \Sigma|F_o{}^2 - F_c{}^2|/\Sigma F_o{}^2$ and $R_w = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^4]^{1/2}$. Atomic scattering factors for non-hydrogen atoms were taken from Cromer's and Waber's tabulation,[42] whereas the hydrogen scattering factors were those of Stewart et al.[43] The anomalous dispersion terms for Ni were included in F_c.[44]

In the initial cycles of refinement the phenyl rings of the fluorene molecule were treated as rigid groups. Upon refinement of all nonphenyl atoms anisotropically and of the carbon atoms of the phenyl rings as isotropically vibrating individual atoms, the agreement indices of 0.092 and 0.137 (on *F*) were obtained. An ensuing difference Fourier synthesis enabled us to locate all hydrogen atoms, even on that *tert*-butyl group which was undergoing a high degree of thermal motion. The hydrogen atoms were included as a fixed contribution in all subsequent refinements, their positions being idealized assuming trigonal and tetrahedral geometries of the phenyl and methyl carbon atoms, respectively, and using a C–H distance of 0.95 Å. Each hydrogen atom was assigned a thermal parameter of 1.0 Å^2 greater than the equivalent isotropic thermal parameter of the carbon atom to which it is attached. In the last two refinement cycles all non-hydrogen atoms were refined anisotropically. The final agreement indices, based on $F_o{}^2$, with 3022 reflections (including $F_o{}^2 \leq 0$) and 253 variables, are $R = 0.076$ and $R_w = 0.129$. The conventional agreement index

Table II. Summary of Crystal Data, Intensity Collection, and Agreement Indices

Compound	$Ni(t\text{-}BuNC)_2(C_{13}H_8N_2)$
Formula weight	417.20 amu
Formula	$C_{23}H_{26}N_4Ni$
a	17.748 (3) Å
b	18.999 (4) Å
c	14.295 (2) Å
V	4820.2 $Å^3$
Z	8
Density	1.149 g/cm^3 (calcd)
Space group	$D_{2h}{}^{15}$-$Pbca$
Crystal dimensions	0.60 × 0.62 × 0.22 mm
Crystal shape	Orthorhombic prism with well developed faces of the forms {100}, {010}, {001}, and {111}
Crystal volume	0.0346 mm^3
Temperature	22 °C
Radiation	Cu $K\alpha_1$ (λ = 1.540562 Å)
μ	12.24 cm^{-1}
Transmission factors	0.639-0.793
Receiving aperture	4.5 × 4.5 mm; 30 cm from crystal
Takeoff angle	3.1°
Scan speed	2° in 2θ/min for $2\theta \leq 105°$ 1° in 2θ/min for $2\theta > 105°$
Scan range	0.9° below $K\alpha_1$ to 0.9° above $K\alpha_2$
Background counts	10 s for $2\theta < 88°$; 20 s for $88° \leq 2\theta \leq 98°$; 40 s for $2\theta > 98°$
2θ limits	2.0-110.0°
Final no. of variables	253
Unique Data Used Including $F_o{}^2 \leq 0$	3022
Unique Data with $F_o{}^2 > 3\sigma(F_o{}^2)$	2095
R (on F^2)	0.076
R_w (on F^2)	0.129
R (on F, $F_o{}^2 > 3\sigma(F_o{}^2)$)	0.046
R_w (on F, $F_o{}^2 > 3\sigma(F_o{}^2)$)	0.063
Error in observation of unit weight	1.79 e^2

on $|F_o|$ for the 2095 reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$ is 0.046. An analysis of $\Sigma w(F_o{}^2 - F_c{}^2)^2$ as a function of $F_o{}^2$, setting angles, and Miller indices shows no unusual trends. The standard deviation of an observation of unit weight is 1.79 e^2. A final difference Fourier synthesis is essentially featureless with the highest peak equal to 0.39 (6) e/$Å^3$.

The final positional and thermal parameters appear in Tables III and IV. Root-mean-square amplitudes of vibration are given in Table V.[45] A listing of the observed and calculated structure amplitudes is available.[45] Entries with $F_o < 0$ are for those reflections having $F_o{}^2 < 0$.

Discussion

(a) Description of the Structure of Ni(*t*-BuNC)₂(diazofluorene). The crystal structure of Ni(t-BuNC)$_2$(diazofluorene) consists of individual monomeric units with no unusual intermolecular contacts (Table VI). Figure 1 shows a stereoscopic view of the packing. A representation of the molecule with the numbering scheme is shown in Figure 2. Figure 3 presents a view of the inner coordination sphere of the molecule showing some of the relevant bond lengths and angles. Figure 4 shows a representation of the diazofluorene ligand with bond lengths and angles.

The diazofluorene molecule may be described as π-bonded to the Ni atom through the N-N multiple bond since the Ni-N distances are essentially equal and the inner coordination about the Ni atom is nearly planar. This coordination is very similar to that observed in other $Ni(t\text{-}BuNC)_2L$ complexes (L = TCNE,[2,46] O_2,[47] PhC≡CPh,[48] PhN=NPh,[26] and t-BuN=C=C(CN)$_2$[8]). The dihedral angle between the Ni-N(1)-N(2) and the Ni-C(14)-C(19) planes is only 5.9 (2)° (Table VII) and thus the inner coordination sphere of the complex is essentially planar, as has been observed in the related $Ni(t\text{-}BuNC)_2$ complexes of t-BuN=C=C(CN)$_2$[8] (dihedral angle 7.9 (3)°), PhN=NPh[26] (dihedral angle 1.2 (3)°), and PhC≡CPh[48] (dihedral angle 2.6 (7)°). The TCNE complex,[46] on the other hand, is significantly more distorted with a corresponding dihedral angle of 23.9 (2)°. There is a notable asymmetry in the Ni coordination not found in these related Ni complexes. Thus the N(2)-Ni-C(19) and N(1)-Ni-C(14) angles differ by 13.1 (3)°. This can be attributed to the highly asymmetric mode of bonding of the diazofluorene molecule, which results in a more crowded environment for one isocyanide ligand (with atom C(19)) than for the other.

The geometries of the isocyanide ligands are normal. The Ni-C distances are equal (1.844 (5) Å) and are comparable with those in other similar structures.[8,26,46-48] Similarly the C-N distances within these ligands are similar to those observed in the related Ni complexes, being close to that expected for a C-N triple bond (ca. 1.15 Å). These ligands are essentially linear with the small deviations from linearity probably resulting from packing forces. The geometries of the *tert*-butyl groups are normal, except for the short C-C distances in the ligand involving atom C(14). These short distances are probably apparent rather than real owing to the large thermal motion of this group.

The diazofluorene molecule is essentially planar (see Table VIII) with the average deviation of an atom from the least-squares plane being only 0.02 Å. Bond lengths and angles within the fluorene part of the molecule (see Figure 4) compare favorably with those in other fluorene derivatives,[49-53] and are in excellent agreement with those in diazofluorene itself.[54]

The mode of coordination of the diazofluorene molecule to the Ni atom is most unusual. Generally azo and diazo ligands are σ-bonded, via a nitrogen atom, to the metal. Thus all reported structures involving the alkyldiazo,[19] the aryldiazo,[9-18] and the monoaryldiazene[20,21] ligands are σ-bonded to the metal or metals.[55] In addition Chatt and co-workers have recently isolated a complex, $WBr(dppe)_2(N_2CH_2)$,[2,56] in which the diazomethane ligand is believed to be σ-bonded to the tungsten atom. With two known exceptions, complexes containing diaryl or dialkyl diazenes,[21-25] coordinated to one metal, are also σ-bonded. These exceptions, $Ni(t\text{-}BuNC)_2(PhNNPh)$[26] and $Ni(PTol_3)_2(PhNNPh)$,[57] are closely related to the present diazofluorene complex. Similarly in $Ni(t\text{-}BuNC)_2((NC)_2CN_2)$ the dicyanodiazomethane ligand is believed to be π-bonded to the Ni atom.[8] Presumably the Ni atom in these complexes is too electron rich to function as a σ electron acceptor and prefers instead to be an electron donor, with the diazoalkane and diaryldiazene ligands functioning as π-acids. In another metal system, $MoCp_2L$ (L = PhNNPh or diazofluorene),[2] the azobenzene and diazofluorene ligands are again believed to be π-bonded.[28] Here the metal is thought to be a strong electron donor. It seems therefore that the unusual π-coordination of these diazo ligands is a consequence of the electronic configuration of the metal. In electron rich metal systems these diazo molecules prefer to act as π-acids, whereas in electron poor metal systems they prefer to function as σ-donors and be σ-bonded through a nitrogen atom lone pair. In two complexes where a diaryldiazene molecule bridges two iron atoms,[58,59] the diazo moiety could be considered to be π-bonded through the N=N group to both Fe atoms. However, the bonding is again thought to be more consistent with a metal-to-nitrogen σ interaction.

Table III. Positional and Thermal Parameters for the Atoms of Ni(t-BuNC)$_2$(diazofluorene)

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
NI	0.03219(3)	0.17927(3)	-0.00700(4)	4.19(3)	3.66(2)	6.48(4)	-0.84(2)	-0.25(3)	-0.63(2)
N(1)	0.03151(19)	0.18929(17)	-0.13738(22)	5.31(14)	4.43(13)	6.67(20)	-1.22(12)	-0.38(14)	-0.04(12)
N(2)	-0.01052(17)	0.14050(16)	-0.11188(20)	3.89(12)	3.54(11)	5.82(17)	-0.37(10)	-0.12(12)	-0.52(11)
N(3)	0.14676(20)	0.28350(18)	0.05684(28)	5.23(15)	3.58(11)	13.0(3)	-0.78(11)	-2.57(18)	-0.65(16)
N(4)	-0.02254(19)	0.13029(17)	0.17973(24)	5.04(14)	4.20(12)	7.04(22)	0.82(11)	0.74(15)	-0.65(14)
C(1)	-0.05737(19)	0.09719(19)	-0.15673(25)	3.53(13)	3.58(12)	6.02(21)	-0.14(11)	-0.31(14)	-1.02(13)
C(2)	-0.09901(19)	0.03993(19)	-0.11565(26)	3.17(12)	3.29(12)	7.27(24)	0.27(10)	0.11(14)	-1.23(15)
C(3)	-0.10179(19)	0.01188(19)	-0.02659(29)	3.81(13)	3.38(13)	8.7(3)	0.10(11)	0.39(16)	-0.57(16)
C(4)	-0.14773(23)	-0.04644(22)	-0.0098(3)	4.66(16)	3.63(13)	11.4(4)	0.40(13)	1.54(21)	0.27(20)
C(5)	-0.18971(23)	-0.07587(22)	-0.0812(4)	3.84(16)	3.50(14)	15.3(5)	-0.72(12)	1.39(24)	-1.49(23)
C(6)	-0.18771(23)	-0.04861(25)	-0.1698(4)	4.13(17)	4.36(17)	12.4(4)	-0.31(14)	0.02(22)	-2.68(22)
C(7)	-0.14336(19)	0.00968(20)	-0.1890(3)	2.96(12)	3.66(13)	9.5(3)	0.13(11)	-0.01(16)	-2.21(17)
C(8)	-0.13045(21)	0.04910(22)	-0.27355(28)	3.83(14)	4.53(15)	7.41(27)	0.38(13)	-0.19(16)	-1.90(17)
C(9)	-0.16040(26)	0.0432(3)	-0.3640(4)	5.02(19)	7.43(24)	9.0(3)	0.17(18)	-1.43(21)	-3.37(24)
C(10)	-0.1357(3)	0.0892(4)	-0.4316(3)	7.75(28)	9.5(3)	7.0(3)	-0.06(24)	-1.32(25)	-1.57(26)
C(11)	-0.0837(3)	0.1414(3)	-0.4116(3)	7.37(26)	7.95(26)	6.9(3)	-0.12(22)	-0.78(24)	-0.11(23)
C(12)	-0.05326(24)	0.14852(25)	-0.3240(3)	5.64(19)	5.70(17)	6.18(25)	-0.07(15)	-0.27(18)	-0.66(18)
C(13)	-0.07634(20)	0.10225(21)	-0.25498(27)	3.69(14)	4.04(14)	6.76(24)	0.36(12)	-0.19(15)	-1.48(16)
C(14)	0.10169(24)	0.24517(21)	0.03201(29)	5.17(17)	3.41(13)	8.15(27)	-0.26(13)	-0.58(18)	-0.18(16)
C(15)	0.2052(3)	0.33160(28)	0.0865(6)	5.65(25)	4.88(25)	21.7(7)	-1.62(18)	-4.3(4)	-2.2(3)
C(16)	0.1851(4)	0.4009(3)	0.0629(8)	12.7(5)	3.45(22)	48.7(14)	-0.96(27)	-14.3(7)	-0.2(5)
C(17)	0.2727(5)	0.3089(5)	0.0543(13)	6.1(4)	10.0(5)	62.(3)	-3.3(4)	0.1(8)	-11.1(11)
C(18)	0.2116(8)	0.3234(8)	0.1881(8)	24.7(10)	28.5(11)	20.8(10)	-17.4(9)	-12.5(9)	0.8(9)
C(19)	-0.00182(23)	0.14662(21)	0.1069(3)	4.42(16)	3.59(14)	7.06(25)	-0.18(13)	-0.12(17)	-0.91(16)
C(20)	-0.05012(28)	0.11208(22)	0.2723(3)	7.14(23)	4.37(16)	7.64(29)	1.20(16)	2.33(21)	0.17(17)
C(21)	-0.0820(4)	0.03861(28)	0.2649(4)	11.9(4)	4.44(19)	16.7(5)	0.29(22)	6.7(4)	0.75(27)
C(22)	-0.11037(28)	0.16560(25)	0.2972(3)	7.21(23)	5.45(19)	9.8(3)	1.61(17)	3.13(23)	0.57(20)
C(23)	0.0163(4)	0.1164(3)	0.3394(3)	9.4(3)	9.1(3)	7.7(3)	3.89(26)	0.48(27)	-0.11(25)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsdquent tables. [b] The form of the anisotropic thermal ellipsoid is: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients × 10^3.

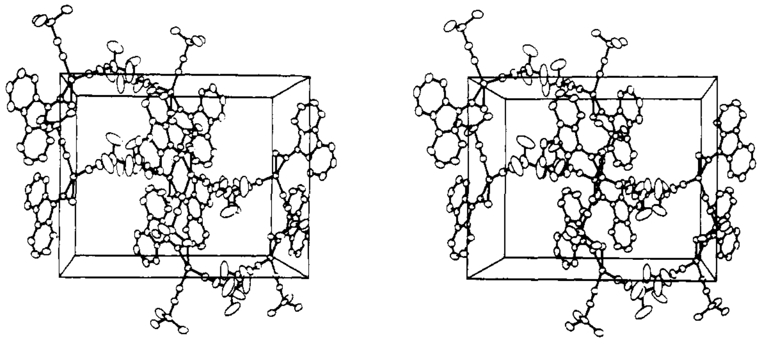


Figure 1. A stereoview of a unit cell of Ni(t-BuNC)$_2$(diazofluorene). The x axis is horizontal to the right, the y axis is perpendicular to the paper going away from the reader, and the z axis is vertical from bottom to top. The vibrational ellipsoids are drawn at the 20% level.

It is interesting that the diazofluorene molecule is coordinated to the Ni atom in the plane of the diazofluorene molecule. Based on steric considerations one might expect instead that the Ni atom would coordinate through the N-N π and π^* orbitals perpendicular to the molecular plane, thereby reducing interactions between the diazofluorene molecule and the t-BuNC ligands. However, a consideration of the molecular orbitals of the diazomethane molecule indicates that the lowest unoccupied molecular orbital (LUMO) is on the two N atoms *in* the molecular plane.[60] This is the π-acceptor orbital of diazomethane. Since the geometry of the LUMO for diazofluorene should be similar, the observed bonding mode is what one would expect. If the $R_2C{=}N{=}$ portion of a diazoalkane is to be involved in the π-coordination to the metal (which is most unlikely in view of the molecular orbital picture), the plane of R_2C should be perpendicular to the plane of the metal complex. Thus on the basis of both molecular orbital theory and the present structural results it is clear that the π-acid center of a diazoalkane molecule is located at the N=N portion of the molecule.

The diazofluorene molecule is asymmetrically bonded to the Ni atom as revealed by the significantly different Ni-N distances (1.874 (3) and 1.834 (3) Å). This asymmetry cannot be attributed to steric effects since, based on repulsions involving the fluorene moiety and the ligands, the opposite tendency would be expected. Alternatively, the longer Ni-N(1) distance could arise from the larger trans influence of the t-BuNC ligand involving atom C(19), since it is more nearly trans to atom N(1) than is the other t-BuNC ligand to atom N(2) (compare angles C(14)-Ni-N(2), 142.8 (2) and C(19)-Ni-N(1), 155.6 (2)°). However on this basis we would expect correspondingly different Ni-C(14) and Ni-C(19) distances. Yet these are identical. It seems more likely that the observed difference in the Ni-N distances reflects the stronger π-acidity of atom N(2) compared with atom N(1). This is reasonable, based on the two most likely contributing valence bond (VB) formulations for the free diazofluorene molecule.

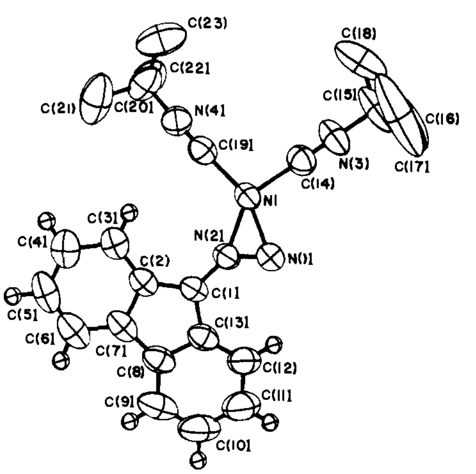


Figure 2. A perspective view of Ni(t-BuNC)$_2$(diazofluorene) showing the numbering scheme. Vibrational ellipsoids are drawn at the 50% level except for hydrogen atoms which are drawn arbitrarily small.

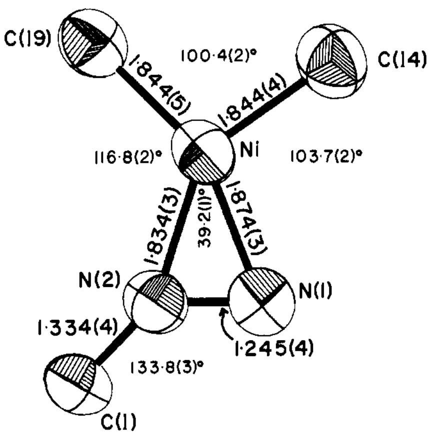


Figure 3. The inner coordination sphere of Ni(t-BuNC)$_2$(diazofluorene) with relevant bond lengths and angles. 50% vibrational ellipsoids are shown.

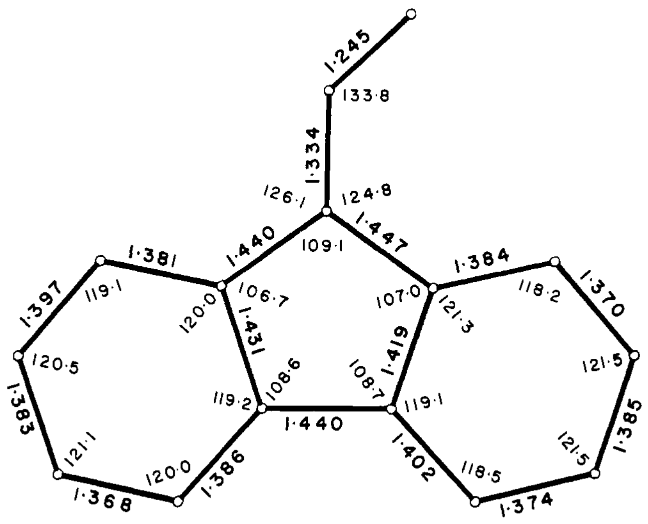


Figure 4. A representation of the diazofluorene ligand showing bond lengths and angles. Estimated standard deviations are about 0.005 Å in bond lengths and 0.5° in bond angles.

Table VI. Selected Distances (Å) in Ni(t-BuNC)$_2$(diazofluorene)

	Bond Distances		
Ni-N(1)	1.874 (3)	C(10)-C(11)	1.385 (7)
Ni-N(2)	1.834 (3)	C(5)-C(6)	1.368 (6)
Ni-C(14)	1.844 (4)	C(9)-C(10)	1.374 (7)
Ni-C(19)	1.844 (5)	C(6)-C(7)	1.386 (6)
N(1)-N(2)	1.245 (4)	C(8)-C(9)	1.402 (5)
N(2)-C(1)	1.334 (4)	C(14)-N(3)	1.139 (5)
C(1)-C(2)	1.440 (5)	C(19)-N(4)	1.147 (5)
C(1)-C(13)	1.447 (5)	N(3)-C(15)	1.446 (5)
C(2)-C(7)	1.431 (5)	N(4)-C(20)	1.453 (5)
C(8)-C(13)	1.419 (5)	C(15)-C(16)	1.405 (8)
C(7)-C(8)	1.440 (5)	C(15)-C(17)	1.354 (10)
C(2)-C(3)	1.381 (5)	C(15)-C(18)	1.466 (12)
C(12)-C(13)	1.384 (6)	C(20)-C(21)	1.510 (7)
C(3)-C(4)	1.397 (5)	C(20)-C(22)	1.518 (6)
C(11)-C(12)	1.370 (6)	C(20)-C(23)	1.522 (7)
C(4)-C(5)	1.383 (6)		
	Nonbonded Distances		
N(1)-H(12)	2.60	N(3)-H2C(18)	2.40
C(19)-H(3)	2.78	N(4)-H2C(21)	2.57
N(3)-H2C(16)	2.53	N(4)-H2C(22)	2.54
N(3)-H2C(17)	2.38	N(4)-H2C(23)	2.54

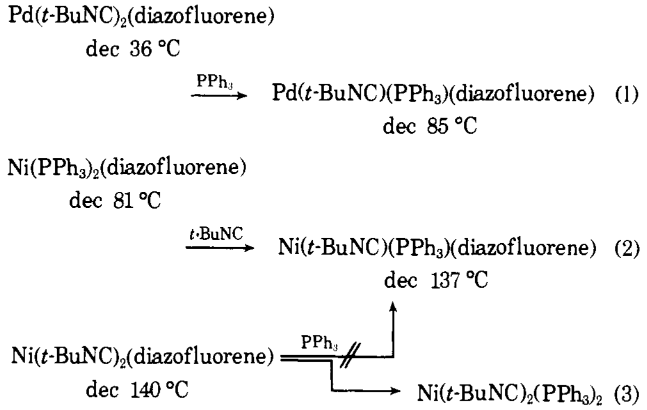
In both cases the inner nitrogen atom (N(2)) is electron poor, whereas the outer nitrogen atom (N(1)) is electron rich. We might therefore expect atom N(2) to be the better electron acceptor. Furthermore, the electron withdrawing properties of the fluorene moiety would enhance the π-acidity of atom N(2). Both these effects would result in a shorter Ni-N(2) bond, as is observed. If we accept the covalent radii of nickel[61] and nitrogen as 1.24 and 0.70 Å, respectively, we conclude that both Ni-N distances (particularly Ni-N(2)) are significantly shorter than that expected for a Ni-N single bond, indicating the importance of the π-accepting properties of the diazofluorene molecule. These Ni-N distances are indeed shorter than those obtained for the closely related complexes Ni(t-BuNC)$_2$(PhNNPh)[26] and Ni(PTol$_3$)$_2$(PhNNPh)[57] (average 1.898 (5) and 1.930 (5) Å, respectively), possibly indicating a stronger π-acidity of the diazofluorene molecule in the present complex.

The N(1)-N(2) distance, at 1.245 (4) Å, corresponds to a N-N double bond and compares well with the distances observed in HN=NH,[62] CH$_3$N=NCH$_3$,[63] and PhN=NPh[64,65] (1.238 (7), 1.254 (3), and 1.244 Å, respectively). The N(1)-N(2) distance is lengthened by 0.120 (6) over that of 1.125 (4) Å in free diazofluorene.[54] The N(2)-C(1) distance, at 1.334 (4) Å, is intermediate between an N-C single and double bond and is close to the value of 1.323 (4) Å observed in diazofluorene. There is a linear N(1)-N(2)-C(1) arrangement in the free molecule.[54] The corresponding angle of 133.8 (3)° in the present complex deviates considerably from linearity and is therefore an indication of the strong π-acidity of the molecule.

(b) Stabilization of Diazoalkane-Nickel(0) and Palladium(0) Complexes with Mixed Auxiliary Ligands. The diazofluorene complex, Ni(t-BuNC)$_2$(diazofluorene) (**1**), prepared by the low-temperature reaction of "Ni(t-BuNC)$_2$" and diazofluorene, is astonishingly thermally stable,[5] decomposing under nitrogen above 140 °C. The thermal stability of Pd(t-BuNC)$_2$(diazofluorene) is less than its Ni analogue (dec 36 °C), but can be increased by replacing one t-BuNC ligand with PPh$_3$ at −78 °C[5] (reaction 1). The reaction of Ni(t-BuNC)$_2$(diazofluorene) with PPh$_3$ does not give the analogous mixed ligand complex, but results instead in the replacement of the diazofluorene molecule by two phosphine ligands (reaction 3). However, replacement of one phosphine ligand in Ni(PPh$_3$)$_2$(diazofluorene) by a t-BuNC ligand does occur, giving a mixed ligand complex (reaction 2). In each of these mixed ligand complexes only one of the two possible geometric isomers is present. Therefore, PPh$_3$ seems to replace regioselectively one of the t-BuNC ligands in Pd(t-BuNC)$_2$(diazofluorene). Based on ground state considerations of the nickel diazofluorene complex (**1**) it is not obvious why this is so, or

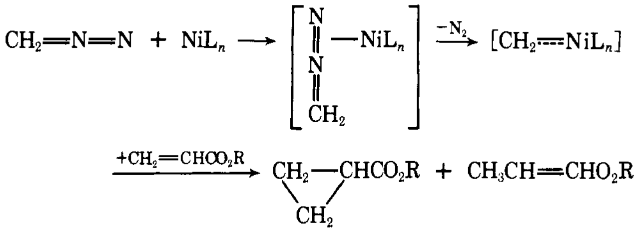
Table VII. Selected Angles (deg) in Ni(t-BuNC)$_2$(diazofluorene)

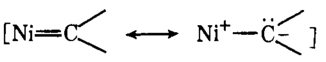
	Bond Angles		
N(1)-Ni-N(2)	39.21 (12)	C(4)-C(5)-C(6)	121.1 (4)
C(14)-Ni-C(19)	100.4 (2)	C(11)-C(10)-C(9)	121.5 (5)
N(1)-Ni-C(14)	103.7 (2)	C(5)-C(6)-C(7)	120.0 (4)
N(1)-Ni-C(19)	155.6 (2)	C(10)-C(9)-C(8)	118.5 (5)
N(2)-Ni-C(19)	116.8 (2)	C(6)-C(7)-C(2)	119.2 (4)
N(2)-Ni-C(14)	142.8 (2)	C(9)-C(8)-C(13)	119.1 (4)
Ni-N(2)-C(1)	153.9 (3)	C(6)-C(7)-C(8)	132.2 (4)
Ni-N(1)-N(2)	68.7 (2)	C(7)-C(8)-C(9)	132.2 (4)
Ni-N(2)-N(1)	72.1 (2)	Ni-C(14)-N(3)	177.0 (4)
N(1)-N(2)-C(1)	133.8 (3)	Ni-C(19)-N(4)	175.9 (4)
N(2)-C(1)-C(2)	126.1 (3)	C(14)-N(3)-C(15)	178.6 (5)
N(2)-C(1)-C(13)	124.8 (4)	C(19)-N(4)-C(20)	177.9 (4)
C(2)-C(1)-C(13)	109.1 (3)	N(3)-C(15)-C(16)	109.8 (5)
C(1)-C(2)-C(7)	106.7 (3)	N(3)-C(15)-C(17)	109.5 (6)
C(1)-C(13)-C(8)	107.0 (4)	N(3)-C(15)-C(18)	106.2 (7)
C(2)-C(7)-C(8)	108.6 (3)	N(4)-C(20)-C(21)	106.4 (4)
C(13)-C(8)-C(7)	108.7 (3)	N(4)-C(20)-C(22)	106.9 (4)
C(1)-C(2)-C(3)	133.3 (3)	N(4)-C(20)-C(23)	107.5 (4)
C(1)-C(13)-C(12)	131.7 (4)	C(16)-C(15)-C(17)	116.2 (9)
C(7)-C(2)-C(3)	120.0 (4)	C(16)-C(15)-C(18)	111.0 (9)
C(8)-C(13)-C(12)	121.3 (4)	C(17)-C(15)-C(18)	103.5 (9)
C(2)-C(3)-C(4)	119.1 (4)	C(21)-C(20)-C(22)	111.8 (4)
C(13)-C(12)-C(11)	118.2 (4)	C(21)-C(20)-C(23)	112.6 (5)
C(3)-C(4)-C(5)	120.5 (4)	C(22)-C(20)-C(23)	111.2 (4)
C(12)-C(11)-C(10)	121.5 (5)		
	Dihedral Angles		
Ni-N(1)-N(2) Ni-C(14)-C(19)	174.1 (2)	C(14)-Ni-N(1) C(19)-Ni-N(2)	175.8 (2)
Ni-N(2)-N(1) C(13)-C(1)-C(2)	8.8 (2)		



even which ligand is being replaced, since both Ni-C distances are identical (1.844 (5) Å), indicating no observable ground state trans influence. Similarly it is not obvious which phosphine ligand is replaced in reaction 2. However, owing to the asymmetric bonding of the diazofluorene molecule to the Ni system we might expect that the more crowded t-BuNC ligand (involving C(19) in the present structure) will be replaced. It is interesting that replacement of a t-BuNC ligand by PPh$_3$ stabilizes the Pd complex, while the opposite is true for the analogous Ni complex. A similar trend has also been observed in the ML$_n$(O$_2$) series. Palladium is a better σ-acceptor than nickel and thus prefers phosphine ligands, which are better σ-donors, to t-BuNC ligands. The opposite is true for nickel.

(c) Cyclopropanation with Diazomethane in the Presence of Ni(0)-Ligand Catalysts. Diazomethane is catalytically decomposed with various nickel(0) or palladium(0) complexes, ML$_n$(M = Ni, Pd; L = t-BuNC, PPh$_3$; n = 2-4), in the presence of an excess of olefins as is shown in the reaction scheme below. The intermediate with the Ni atom π-bonded to the diazo group is proposed as the initial step based on the analogy with diazofluorene, as has been discussed earlier. Typical results are summarized in Table I. Although good yields of the cyclopropanation products are obtained with methyl acrylate and ethyl acrylate, only trace yields are obtained when alkyl- or arylethylenes (e.g., 1-hexene, cyclohexene, or styrene) are used. Cyclopropanation by the Ni(0) complexes consistently does not occur with alkyl-substituted olefins. These results suggest a nucleophilic attack of a carbenoid carbon atom on the electronegative olefins. The nucleophilicity of the carbenoid carbon atom is understood as being caused by polarization of the Ni^0=CR$_2$ moiety.[4,66]





Further it is of interest to observe pyrazoline formation in the absence of nickel(0) complexes. Thus diazomethane readily reacts with olefins having electron-withdrawing substituents (e.g., CO$_2$R or CN) to give the 2-pyrazoline derivatives via 1,3-dipolar addition. These 2-pyrazolines, once formed, do not eliminate molecular nitrogen upon contact with Ni(PPh$_3$)$_4$ or Ni(t-BuNC)$_2$ even at 100 °C. Therefore, the cyclopropanation products formed in the Ni(0) catalyzed reactions of diazomethane and olefins are not derived from the ring contraction of the corresponding 2-pyrazolines. They must instead be derived from the direct reaction of nickel(0)-carbene complexes with the olefin. This inference is supported by the increase in yields of the cyclopropanation product with the increase in

Table VIII. Weighted Least-Squares Planes

Plane Equation: $Ax + By + Cz - D = 0$, with x, y, z in Orthorhombic Coordinates

Plane no.	A, Å	B, Å	C, Å	D, Å
1	13.508	−11.531	−3.270	−1.424
2	13.075	−11.951	−3.547	−1.320
3	13.215	−11.913	−3.273	−1.401
4	13.301	−11.753	−3.373	−1.381
5	12.772	−13.172	−0.547	−1.950

Deviations from the Planes, Å

Atom	Plane no. 1	2	3	4	5
Ni					0.0036 (6)
N(1)				0.039 (3)	−0.066 (3)
N(2)				−0.033 (3)	0.026 (3)
C(1)			−0.002 (3)	0.005 (3)	
C(2)	0.005 (3)		−0.005 (3)	−0.015 (3)	
C(3)	−0.001 (3)			−0.022 (3)	
C(4)	−0.004 (4)			−0.005 (4)	
C(5)	0.002 (4)			0.024 (4)	
C(6)	0.004 (4)			0.029 (4)	
C(7)	−0.006 (3)		0.009 (3)	−0.002 (3)	
C(8)		−0.002 (4)	−0.013 (4)	−0.008 (4)	
C(9)		−0.003 (5)		−0.032 (5)	
C(10)		0.010 (6)		−0.016 (6)	
C(11)		−0.005 (5)		−0.006 (5)	
C(12)		−0.002 (4)		0.020 (4)	
C(13)		0.004 (4)	0.009 (4)	0.024 (4)	
C(14)					0.002 (4)
C(19)					−0.063 (4)

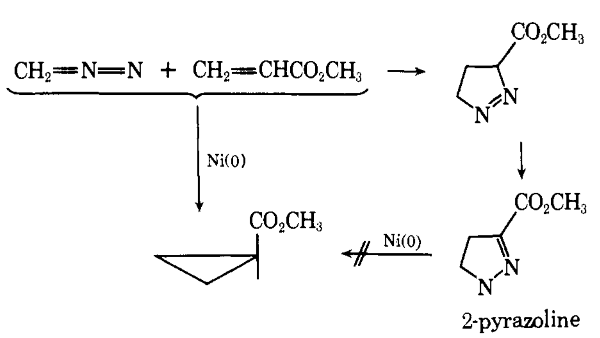
Dihedral Angles between Planes

Plane A	Plane B	Angle, deg
1	2	2.19
1	3	1.49
2	3	1.19

Table IX. Percentage Yield of Products from the $Ni(PPh_3)_4$-Catalyzed Reaction between Diazomethane and Methyl Acrylate[a]

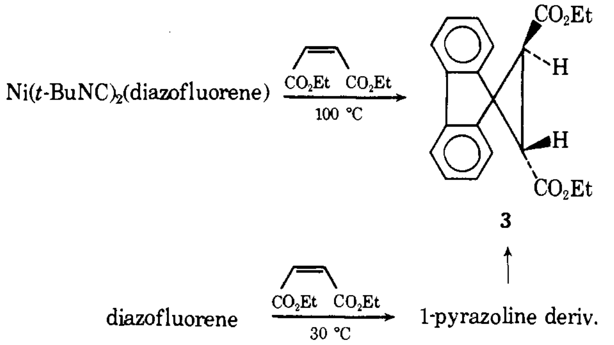
Molar ratio (catalyst/acrylate)	Methyl cyclopropane-carboxylate, %	Methyl crotonate, %
0.025	21.6	33.4
0.122	72.0	7.1
0.2	72.6	9.5
0.5	77.0	6.7
1	75.4	1.0

[a] In ether under nitrogen for 1.5 h.



catalyst concentration (Table IX). In the absence of the catalyst the cyclopropanation and the insertion reactions[67] leading to methyl crotonate are competitive. The presence of a molar amount of the Ni(0) complex almost completely suppresses the latter reaction.

(d) Reaction of the Diazofluorene–Nickel(0) Complexes. In contrast to the ligand replacement reactions of the complexes by strong π-acids (e.g., O_2), diethyl maleate or ethyl acrylate does not displace η^2-diazofluorene at room temperature. Weak interaction, presumably via the double bond of the maleate, was detected by the ^1H NMR spectra of a mixture of the maleate and Ni(*t*-BuNC)₂(diazofluorene) (see Experimental Section). Reaction of diethyl maleate with the diazofluorene complex *does not occur at 30 °C*, but on heating at 100 °C an appreciable amount of a *trans*-cyclopropane derivative[68] **3** was



obtained. On the other hand, the thermal reaction of free diazofluorene with diethyl maleate at room temperature readily gives a 1-pyrazoline derivative by 1,3-dipolar addition. Nitrogen elimination by thermal decomposition of the pyra-

Table X. Isocyanide Stretching Frequencies and Inter-Isocyanide Ligand Angles in Complexes, Ni(*t*-BuNC)$_2$(AB)

AB	Ni-C, Å[a]	$\nu_{N\equiv C}$, cm^{-1}	φ, deg[b]
PhC≡CPh	1.83 (3)	2138, 2110[d]	106.3 (16)[g]
PhN═NPh	1.841 (5)	2168, 2140[d]	101.8 (2)[h]
$C_{13}H_8N_2$	1.844 (4)	2180, 2158[e]	100.4 (2)[i]
t-BuN═C═C(CN)$_2$	1.85 (4)[c]	2180, 2160[f]	105.4 (2)[f]
(CN)$_2$C═C(CN)$_2$	1.866 (5)	2194, 2179[d]	98.9 (2)[j]
O_2	1.84 (1)	2196, 2178[d]	91.8 (5)[k]

[a] Ni-C distances involve the *t*-BuNC ligands. [b] φ is the C-Ni-C angle between the two isocyanide ligands. [c] The two Ni-C distances are significantly different. The value quoted is the mean. [d] Reference 69 (and references therein). [e] Reference 5. [f] Reference 8. [g] Reference 48. [h] Reference 26. [i] This work. [j] Reference 46. [k] Reference 47.

zoline proceeds very slowly at 30 °C to give the same *trans*-cyclopropane derivative.[68] Therefore, the *trans*-cyclopropane derivative obtained from the nickel complex may result from the thermal reaction of free diazofluorene with diethyl maleate. Thermal dissociation of diazofluorene from the nickel complex is thereby implicated.

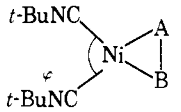
It seems as though the π-complexation of diazofluorene (η^2-coordination through N═N) hinders its dipolar addition to olefins and the resultant formation of the pyrazoline derivatives. With diazomethane, however, the absence of the pyrazoline derivatives results from the rapid reaction of diazomethane with Ni or Pd catalysts to produce the carbene, which then reacts with ethyl acrylate, for example, to form cyclopropane carboxylate and ethyl crotonate (see Table I). In the absence of these Ni and Pd catalysts only 2-pyrazoline carboxylate results and remains as such at that temperature. Thus the presence of Ni or Pd complexes hinders the formation of the pyrazoline derivatives of both diazofluorene and diazomethane, but for different reasons.

(e) Thermal Decomposition of Diazofluorene-Palladium(0) Complexes in the Presence of Olefins. Reaction of the diazofluorene-palladium complex, Pd(PPh$_3$)$_2$(diazofluorene), with excess dimethyl maleate at −70 °C followed by warming to 80 °C in toluene gives the same cyclopropane derivative, 3 (21%). The use of *t*-BuNC as a ligand in the same reaction gives only a small amount (3.8%) of the cyclopropane mixed with the *N-tert*-butylfluorenylideneketenimine (23%), bisfluorenylideneazine (4.8%), and *N-tert*-butyl-9-fluorenecarboxamide (9%). The differences in the reactions with *t*-BuNC and phosphine ligands probably result from the lower stability of the isocyanide complexes; subsequent competing reactions between the coordinated diazofluorene and the *t*-BuNC ligands result in the ketenimine. The amide probably results from hydrolysis of the ketenimine on the silica gel column. The azine results from the usual solution chemistry of free diazofluorene.

(f) The π-Acidity of the Diazofluorene Ligand. Since several complexes, Ni(*t*-BuNC)$_2$(AB), have been structurally characterized, information about the relative π-acidities of the π-ligands, AB, should be deducible from these results. Obvious parameters for comparison are the Ni-A and Ni-B distances, since a stronger π-acid would presumably be more tightly bound to the Ni atom and shorter distances would result. Unfortunately differences in these distances arise both from changes in π-acidity and in covalent radii. Alternatively, the relative increase in the A-B bond length upon coordination should give a measure of the π-acidity.[69] Again, however, the different atoms and covalent radii confuse this measure. Also of potential utility as an indication of the π-acidity of AB is the geometry of the Ni(*t*-BuNC)$_2$ core, a feature which is common to all of these complexes. As the π-acidity of AB increases, less electron density is available for π back-bonding onto the *t*-BuNC ligands, with concomitant lengthening of the Ni-C distances (of the *t*-BuNC ligands) and contraction of the C≡N distances. Owing to the uncertainty in the C≡N distances, arising from the high thermal motion of the *t*-BuNC ligands, these distances are not generally useful. Based on the Ni-C distances (see Table X) the following order of increasing π-acidity of AB is obtained: PhC≡CPh < O_2 < PhN═NPh < diazofluorene < *t*-BuN═C═C(CN)$_2$ < TCNE. Apart from the position of O_2[70] (we would expect it to be near TCNE), the above series is in line with our expectations. Although the differences in Ni-C bond lengths are not all significant, the trend is obvious.

A sensitive indication of the relative π-acidities of the π-ligands is the C≡N stretching frequency of the *t*-BuNC ligands. By the same argument that predicts a shorter C≡N distance as the π-acidity of AB increases, a higher value of $\nu_{C\equiv N}$ is also expected. Table X shows a compilation of the $\nu_{C\equiv N}$ for the complexes which have been structurally characterized (a more complete tabulation is available in ref 69). Values of $\nu_{C\equiv N}$ of about 2000 cm^{-1} correspond formally to Ni(0) systems, whereas values near 2200 cm^{-1} correspond to Ni(II).[69] This indicates the importance of π bonding in stabilizing these complexes, since in all examples from one to two electrons, in a formal sense, have been transferred to the π-ligand (formally $\simeq$1.8 e for diazofluorene). Table X has the molecules listed in order of increasing π-acidity with TCNE and O_2 being the strongest π-acids. Diazofluorene, with $\nu_{C\equiv N}$ of 2180 and 2158 cm^{-1}, can also be regarded as a strong π-acid. Apart from the position of O_2, this order of π-acidity is identical with that derived from the Ni-C distances. However, the position of O_2 in this series, based on the $\nu_{C\equiv N}$ values, is more reasonable.

Also shown in Table X are the angles, φ, between the *t*-BuNC ligands. An interesting trend, which parallels the C≡N stretching frequencies, is obvious in these angles. With the exception of *t*-BuN═C═C(CN)$_2$, all complexes show a decrease in φ with increasing $\nu_{C\equiv N}$ and therefore with increasing π-acidity of AB. This variation in φ is significant and probably does not result from packing effects. It is tempting, then, to interpret this correlation in terms of repulsion between the bonding electron pairs. With increasing π-acidity of AB, less electron density is back-donated onto the *t*-BuNC ligands. This would result in less repulsion between the bonding orbitals of these ligands and hence a decrease in the value of φ. However, a more detailed discussion of this structural feature must await the results of molecular orbital calculations, now in progress. A similar structural trend is also observed in a series of M(PR$_3$)$_2$(AB) complexes,[71-87] as will be discussed in detail separately.



Conclusions

There are significant differences in the reaction chemistry of diazomethane and diazofluorene with olefins. The former seems to react with olefins via a carbene pathway, forming the cyclopropane derivative readily in the presence of Ni(0) or Pd(0) catalysts. In the absence of Ni or Pd compounds, diazomethane and substituted olefins form the 2-pyrazoline derivatives, which do not yield the cyclopropane derivatives via ring contraction, even in the presence of Ni or Pd catalysts. On the other hand, diazofluorene seems to react via a 1-pyrazoline intermediate, forming the cyclopropane derivative by ring contraction of the pyrazoline. Thus the cyclopropane derivative is formed at 30 °C even in the absence of the metal compounds. The retardation of the cyclopropane reaction when ML_2(diazofluorene) compounds are reacted with olefins (the reaction proceeds slowly at 100 °C) indicates that prior dissociation of the diazofluorene may be required before reaction with the olefin can occur. It seems then that the presence of Ni(0) or Pd(0) has the opposite effect on the reaction chemistry of these two diazoalkanes. One wonders then if the structure of Ni(*t*-BuNC)$_2$(diazofluorene) can be used as an aid to generalize about the reactions of diazoalkanes. The answer to this, we believe, is yes—but with caution. We believe that diazomethane probably reacts initially via coordination of the N-N bond to the metal. However, the diazomethane-metal complex is highly unstable, as witnessed by the evolution of N_2 in the reaction of $Ni(PPh_3)_4$ and CH_2N_2 even at −78 °C. The carbene thus formed reacts readily with the olefins, producing the cyclopropane derivatives directly. The stabilizing effect of the fluorenyl group is apparent, however, allowing isolation of the diazofluorene complex, Ni(*t*-BNC)$_2$(diazofluorene). A similar, but less stable, complex has also been isolated with dicyanodiazomethane. Since the diazofluorene complexes are stable, the "normal" reactions between diazofluorene and olefins are retarded and the mixture must be heated to 100°C to obtain the cyclopropanation product. Therefore the key to the differences in the reactions of these diazoalkanes is the stability of the metal-diazoalkane complex involved, with the more stable diazoalkane complex forming the cyclopropanation product more slowly.

A knowledge of the structure of Ni(*t*-BuNC)$_2$(diazofluorene) has also proved useful in understanding more about the coordination of unsaturated molecules to transition metals. Diazo and diazene molecules have only rarely been found to be π-bonded to metals, the present diazofluorene being one example. The electron configuration of the metal is important, with electron rich metals tending to act as electron donors and electron poor metals acting as electron acceptors. We therefore expect to observe these diazo molecules π-bonded to electron rich metals and σ-bonded to electron poor metals. In the few examples containing π-bonded diazo and diazene molecules the metals do seem to be electron rich.

A comparison of the geometries of other related complexes, $ML_2(AB)$, has shown that much can be learned about the π-accepting ability of AB by observing changes in the other ligands. When L is *t*-BuNC, the C≡N stretching frequency is a useful measure of the π-acidity of AB, with higher $\nu_{C\equiv N}$ values observed for stronger π-acids. Although the M-C distances of the *t*-BuNC ligands also give a measure of this, the differences are barely significant and not generally as useful. A useful parameter in this regard, especially when no spectroscopically convenient ligand, such as *t*-BuNC, is present, is the L-M-L angle, which decreases markedly as the π-acidity of AB increases.

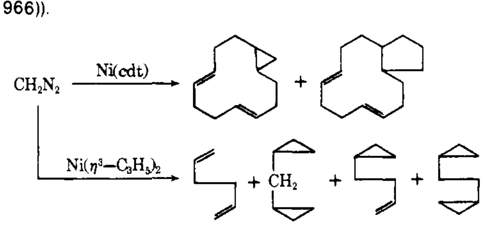
The present study has therefore provided considerable information on the bonding of diazoalkanes to metals and the reaction chemistry of diazoalkanes in the presence of metal complexes.

Acknowledgments. This work was supported by the National Science Foundation and the Japanese Society for the Promotion of Science under the Japan-U.S. Cooperative Science Program (6R021/OIP75-09438). The authors acknowledge the experimental assistance of Dr. Yoshitaka Tatsuno, Mr. Masafumi Terada, and Mr. Akira Konishi. M.C. wishes to thank the National Research Council of Canada for a Postdoctoral Fellowship.

Supplementary Material Available: a listing of the idealized positional coordinates of the hydrogen atoms (Table IV), the root-mean-square amplitudes of vibration (Table V), and the observed and calculated structure amplitudes (23 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Osaka University; (b) Northwestern University.
(2) Abbreviations: L = neutral ligand, R = organic group, *t*-Bu = *tert*-butyl, Ph = C_6H_5, Tol = *p*-$C_6H_4CH_3$, Et = C_2H_5, TCNE = tetracyanoethylene, dppe = $Ph_2PCH_2CH_2PPh_2$, Cp = cyclopentadienyl.
(3) D. J. Cardin, B. Cetinkaya, S. Cetinkaya, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 514 (1973).
(4) R. Noyori, *Tetrahedron Lett.*, 1691 (1973).
(5) S. Otsuka, A. Nakamura, T. Koyama, and Y. Tatsuno, *Justus Liebigs Ann. Chem.*, 626 (1975), and references cited therein.
(6) The reaction of diazomethane with Ni(cdt) (cdt = 1,5,9-cyclodecatriene) or Ni(η^3-C_3H_5)$_2$ has been reported to give cyclopropanation or ligand coupling products (P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. 1, Academic Press, New York, N.Y., 1974, pp 257 and 340; B. Bogdanovic, M. Kröner, and G. Wilke, *Justus Liebigs Ann. Chem.*, **199**, 1 (1966)).



(7) The bonding scheme between the metals and the diazo compounds was inferred[5] on the basis of the symmetry properties, energy levels, and orbital extension of the relevant molecular orbitals of the components. η^2-Coordination through the N═N moiety to an essentially zero-valent metal, in a planar manner, has been suggested. The proposed structure must be verified by x-ray analysis in order to give some credit to this inference by the molecular orbital approach. Unfortunately, the difficulty in obtaining good crystals has prevented the x-ray analysis so far.
(8) D. J. Yarrow, J. A. Ibers, Y. Tatsuno, and S. Otsuka, *J. Am. Chem. Soc.*, **95**, 8590 (1973).
(9) A. P. Gaughan, B. L. Haymore, J. A. Ibers, W. H. Myers, T. E Nappier, and D. W. Meek, *J. Am. Chem. Soc.*, **95**, 6859 (1973).
(10) S. Krogsrud and J. A. Ibers, *Inorg. Chem.*, **14**, 2298 (1975).
(11) G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Crystallogr., Sect. B*, **27**, 725 (1971).
(12) (a) J. A. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg *Inorg. Chem.*, **12**, 1676 (1973); (b) B. L. Haymore and J. A. Ibers, *ibid.*, **14**, 3060 (1975).
(13) R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Galbraith, and B. L. Shaw, *J. Am. Chem. Soc.*, **96**, 260 (1974); V. F. Duckworth, P. G. Douglas, R. Mason, and B. L. Shaw, *Chem. Commun.*, 1083 (1970).
(14) B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, **14**, 1369 (1975).
(15) M. Cowie, B. L. Haymore, and J. A. Ibers, *Inorg. Chem.*, **14**, 2617 (1975).
(16) E. W. Abel, C. A. Burton, M. R. Churchill, and K.-K. G. Lin, *J. Chem. Soc., Chem. Commun.*, 268 (1974).
(17) M. Cowie, B. L. Haymore, and J. A. Ibers, *J. Am. Chem. Soc.*, **98**, 7608 (1976).
(18) D. Sutton, *Chem. Soc. Rev.*, **4**, 443 (1975).
(19) V. W. Day, T. A. George, and S. D. A. Iske, *J. Am. Chem. Soc.*, **97**, 4127 (1975).
(20) S. D. Ittel and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4804 (1974).
(21) B. L. Haymore and J. A. Ibers, *J. Am. Chem. Soc.*, **97**, 5369 (1975).
(22) A. L. Balch and D. Petridis, *Inorg. Chem.*, **8**, 2247 (1969), and references cited therein.
(23) G. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970), and references cited therein.
(24) I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, **13**, 28 (1960).
(25) M. I. Bruce, R. C. F. Gardner, B. L. Goodall, P. G. A. Stone, R. J. Doedens, and J. A. Moreland, *J. Chem. Soc., Chem. Commun.*, 185 (1974).
(26) (a) R. S. Dickson, J. A. Ibers, S. Otsuka, and Y. Tatsuno, *J. Am. Chem. Soc.*, **93**, 4636 (1971); (b) R. S. Dickson and J. A. Ibers, *ibid.*, **94**, 2988 (1972).
(27) S. D. Ittel and J. A. Ibers, *J. Organomet. Chem.*, **57**, 389 (1973).
(28) A. Nakamura, M. Aotake, and S. Otsuka, *J. Am. Chem. Soc.*, **96**, 3456 (1974).
(29) S. Otsuka, A. Nakamura, and Y. Tatsuno, *J. Am. Chem. Soc.*, **91**, 6994 (1969).
(30) R. A. Schunn, *Inorg. Synth.*, **13**, 124 (1972).
(31) P. Heimbach, *Angew, Chem., Int. Ed. Engl.*, **3**, 648 (1964).
(32) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).
(33) D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972).
(34) F. G. Mann and D. Puride, *J. Chem. Soc.*, 1549 (1935).

(35) H. Pechman, *Ber.*, **27**, 1888 (1894); **28**, 855 (1895).
(36) W. E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).
(37) N. E. Serle, "Organic Syntheses", Collect. Vol. 4, Wiley, New York, N.Y., 1963, p 424.
(38) C. M. McClosky and G. H. Coleman, "Organic Syntheses", Collect. Vol. 3, Wiley, New York, N.Y., 1952, p 221.
(39) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).
(40) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).
(41) The Northwestern absorption program, AGNOST, includes the Coppens–Leiserowitz–Rabinowvitch logic for Gaussian integration. In addition to various local programs for the CDC 6400 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Johnson's ORTEP thermal ellipsoid plotting program, and Busing and Levy's ORFFE error function program. Our full-matrix, least-squares program, NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program. The diffractometer was run under the disk-oriented Vanderbilt system (P. G. Lenhert, *J. Appl. Crystallogr.*, **8**, 568 (1975)).
(42) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A.
(43) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(44) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(45) Supplementary material.
(46) J. K. Stalick and J. A. Ibers, *J. Am. Chem. Soc.*, **92**, 5333 (1970).
(47) M. Matsumoto and K. Nakatsu, *Acta Crystallogr., Sect. B*, **31**, 2711 (1975).
(48) R. S. Dickson and J. A. Ibers, *J. Organomet. Chem.*, **36**, 191 (1972).
(49) D. M. Burns and J. Iball, *Proc. R. Soc. London*, **227**, 200 (1955).
(50) J. Silverman, A. P. Krukonis, and N. F. Yannoni, *Acta Crystallogr.*, **23**, 1057 (1967).
(51) J. Silverman, A. P. Krukonis, and N. F. Yannoni, *Acta Crystallogr., Sect. B*, **24**, 1481 (1968).
(52) D. L. Dorset, A. Hybl, and H. L. Ammon, *Acta Crystallogr., Sect. B*, **28**, 3122 (1972).
(53) J. Silverman, A. P. Krukonis, and N. F. Yannoni, *Acta Crystallogr., Sect. B*, **29**, 2022 (1973).
(54) T. Tulip, and J. A. Ibers, unpublished results. See also P. W. R. Corfield, W. C. Hamilton, J. A. Ibers, D. F. Koenig, and S. J. La Placa, American Crystallographic Meeting, Atlanta, Georgia, 1967, Abstract No. B8.
(55) W. A. Herrmann, M. L. Ziegler, and K. Weidenhammer, *Angew. Chem., Int. Ed.*, **15**, 368 (1976).
(56) J. Chatt, personal communication.
(57) S. D. Ittel and J. A. Ibers, *J. Organomet. Chem.*, **57**, 389 (1973).
(58) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **8**, 2709 (1969).
(59) R. J. Doedens, *Inorg. Chem.*, **9**, 429 (1970).
(60) W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973.
(61) J. P. Jesson and E. L. Muetterties, "Chemist's Guide to Basic Chemical and Physical Data", Marcel Dekker, New York, N.Y., 1969.
(62) A. Trombetti, *Can. J. Phys.*, **46**, 1005 (1968).
(63) C. H. Chang, R. F. Porter, and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 5313 (1970).
(64) C. J. Brown, *Acta Crystallogr.*, **21**, 146 (1966); of the two molecules in the asymmetric unit, one is ordered, one is disordered. The bond lengths for the ordered molecule are quoted.
(65) C. J. Brown, *Acta Crystallogr.*, **21**, 153 (1966).
(66) C. Rüchardt and G. Schrauzer, *Chem. Ber.*, **93**, 1840 (1960).
(67) The term "insertion" does not have any mechanistic implications.
(68) The authentic sample was prepared by the reaction of dimethyl fumarate (2.3 g) with diazofluorene (0.75 g) in benzene (25 ml) at room temperature for 2 days. Colorless needles (hexane), mp 139–140 °C.
(69) S. D. Ittel and J. A. Ibers, *Adv. Organomet. Chem.*, **14**, 33 (1976).
(70) The bonding nature of MO_2 differs from that of MA_2 ($A_2 = HC{\equiv}CH$, $HN{=}NH$) as revealed by molecular orbital calculations (MINDO, ASMO, SCF). K. Tatsumi, Ph.D. Thesis, Osaka University, 1976.
(71) P. T. Cheng and S. C. Nyburg, *Can. J. Chem.*, **50**, 912 (1972).
(72) S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, **12**, 2290 (1973).
(73) J. M. Baraban and J. A. McGinnety, *Inorg. Chem.*, **13**, 2864 (1974).
(74) N. Yasuoka, M. Morita, Y. Kai, and N. Kasai, *J. Organomet. Chem.*, **90**, 111 (1975).
(75) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 1767 (1970).
(76) M. Kadonaga, N. Yasuoka, and N. Kasai, *Chem. Commun.*, 1597 (1971).
(77) (a) M. E. Jason, Ph.D. Dissertation, Yale University, 1976; (b) M. E. Jason, J. A. McGinnety, and K. B. Wiberg, *J. Am. Chem. Soc.*, **96**, 6531 (1974).
(78) J. M. Baraban and J. A. McGinnety, *J. Am. Chem. Soc.*, **97**, 4232 (1975).
(79) C. Panattoni, R. Graziani, C. Bandoli, D. A. Clemente, and U. Belluco, *J. Chem. Soc. B*, 371 (1970).
(80) J. N. Francis, A. McAdam, and J. A. Ibers, *J. Organomet. Chem.*, **29**, 131 (1971).
(81) M. A. Bennett, G. B. Robertson, P. O. Whimp, and T. Yoshida, *J. Am. Chem. Soc.*, **93**, 3797 (1971).
(82) J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organomet. Chem.*, **7**, 9 (1967).
(83) A. McAdam, M. N. Francis, and J. A. Ibers, *J. Organomet. Chem.*, **29**, 149 (1971).
(84) G. Bombieri, E. Forsellini, C. Panattoni, R. Graziani, and G. Bandoli, *J. Chem. Soc. A*, 1313 (1970).
(85) B. W. Davies and N. C. Payne, *Inorg. Chem.*, **13**, 1848 (1974).
(86) C. G. Biefeld, H. A. Eick, and R. H. Grubbs, *Inorg. Chem.*, **12**, 2166 (1973).
(87) F. Cariati, R. Mason, G. B. Mason, and R. Ugo, *Chem. Commun.*, 408 (1967).