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Low-Valent Nickel Complexes of Substituted Diazenes

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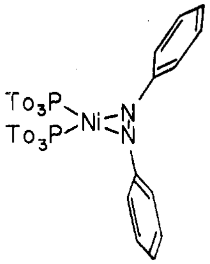
Substituted diazenes react with zerovalent nickel phosphine complexes to form π complexes or to eliminate dinitrogen to form nickel(II) species. Possible alternative mechanisms for the photochromic behavior of an azobenzene π complex are suggested. Several cyano- and alkyl-substituted diazenes have been shown to eliminate dinitrogen and oxidatively add to the Ni(0) complexes. Evidence is presented to suggest that oxidative addition takes place through a π intermediate. A new complex of bis(*p*-methylbenzoyl)diazene exhibits a fluxional behavior between square-planar and tetrahedral coordination about the nickel atom.

Introduction

There has been great interest in the coordination chemistry of diazenes (azo compounds) since it was discovered that they could be used for dyes and that the introduction of metal ions could modify the properties of those dyes.[1] More recently it was discovered that azobenzene could form π complexes with nickel(0).[2-5] Since that time, we have been investigating the nature of diazene complexes through structural and spectroscopic techniques.[5-9] The π complexes of azobenzene, such as I, were shown to be trigonal planar,[5,6] if the diazene is considered to be monodentate, with the two nitrogen atoms equidistant from the metal. Comparison with an isoelectronic olefin complex of *trans*-stilbene[8] indicates that the diazene is bound more tightly to the metal, presumably as a result of increased π back-bonding. The structure[9] of a platinum(II) complex of phenyldiazene demonstrates that π back-bonding is not necessarily important in complexes where the diazene is unsymmetrically σ bonded through one of the nitrogen lone pairs.



I

It has been proposed that the decomposition of diazenes to dinitrogen and free radicals goes through a cis intermediate.[10,11] Because certain diazenes are important free-radical initiators, there has been a considerable amount of work in this area.[12] The decomposition, which can be thermal or photochemical, has been shown to be accelerated by the presence of Cu(II) ions.[13] With more stable diazenes, such as azobenzene, photochromic behavior,[1,14,15] in which the trans species is converted to the cis species and then slowly decays back to the trans species without decomposition and evolution of dinitrogen, is observed.

Though the unsubstituted parent molecule, diazene, is not readily available,[16] diazenes with a wide variety of substituents are available. Transition metal complexes of azopyridines have been reported. The 4,4'-azopyridines have been shown to behave as substituted pyridines,[17] but 2,2'-azopyridine has been shown[18] to form several types of complexes involving the pyridines and the azo bridge. The mode of bonding of the azopyridine to the metal has been correlated with the infrared spectra of the complexes.[18]

Arylcyanodiazenes[19] and dicyanodiazene[20,21] have been reported. Dicyanodiazene has been shown to form 1:1 and 2:1 complexes with chlorobis(triphenylphosphine)carbonyliridium.[22] It is assumed that these are π-type complexes where the diazene is bonded in a manner similar to that of tetracyanoethylene.[23] Dibenzoyldiazene has been shown to form a variety of transition metal complexes[24-26] including one with platinum(0) in which the diazene is bonded through the lone-pair electrons of one nitrogen atom and one oxygen atom. The complex may be formally regarded as a Pt(II) complex of an enolized dibenzoylhydrazido moiety.[7]

None of the chemistry sketched above has been investigated using Ni(0) systems. The present work presents such an investigation, and several interesting differences and similarities with Pt(0) and Ir(I) chemistry are noted.

Experimental Section

Bis(1,5-cyclooctadiene)nickel, Ni(COD)$_2$, was prepared by standard methods.[27] All phosphines were commercially available and were used as received. All substituted azobenzenes were commercially available or were prepared from the appropriate nitrobenzenes by modifications of the standard method.[28] The 1-*p*-tolyl-2-cyanodiazene[19] was prepared by the reaction of sodium cyanide with *p*-tolyldiazonium chloride in water followed by extraction with ether. Dicyanodiazene (DCND) was prepared by a modification[22] of the literature method.[20,21] The preparation of dicyanodiazene is very hazardous because of the explosive nature of its precursor, cyanogen azide. The similarity between the azo compounds used and 4-dimethylaminoazobenzene, which appears on the OSHA list of carcinogenic compounds, should be noted.

Solvents for all reactions involving low-valent nickel species were free of oxygen and water. All reactions were carried out under an atmosphere of argon. Hydrocarbon mull infrared spectra were recorded on a Beckman IR-9 spectrometer. Raman spectra were recorded using a Spex 1400-II double monochromator, a Spectra-Physics laser, and a spinning-sample technique. Electronic spectra were recorded on a Cary 14 spectrophotometer using toluene as solvent and a cell specially designed for handling air-sensitive compounds. Nmr spectra were recorded on a Perkin-Elmer R-20B spectrometer (60 MHz) using serum-capped tubes and deuteriobenzene. Melting points were determined in sealed, evacuated capillaries and are uncorrected.

Preparation of Ni(PEt$_3$)$_2$(ToN═NTo)[29] (II). Ni(COD)$_2$ (2.23 g, 8.10 mmol) and ToN═NTo (1.70 g, 8.10 mmol) were placed in a Schlenk tube at room temperature and pentane (15 ml) was injected. PEt$_3$ (2.4 ml, 16.2 mmol) was quickly injected into the stirred suspension and the mixture immediately turned dark red. After 20 min the sample was collected by vacuum filtration and washed with several portions of cold pentane. Recrystallization from diethyl ether resulted in a highly crystalline, dark red product. Compounds III–VI were prepared similarly. Compounds VII and VIII were prepared in the same manner using toluene as a solvent and a reaction time of 6 hr. The n → π* transitions of compounds V and VI were determined using a 1-mm cell instead of the usual 10-mm cell owing to dissociation at the more dilute concentration. The n → π* transition of VII could not be determined because of extensive dissociation. Concentrated solutions of VII are red but unlike solutions of the other complexes, which turn rose or pink upon dilution, the solution turns orange, indicating dissociation of complex VII to the free azobenzene. Melting points and spectral data for these compounds are presented in Table I.

Analytical results were satisfactory and are presented for all compounds in Table II.[30]

Preparation of Ni(PTo$_3$)(Ph^{15}N═^{15}NPh). Enriched (98.7%)

Table I. Decomposition Points, Electronic Spectra, and Proton Nmr Spectra for the Complexes $Ni(PEt_3)_2$(diazene)

			$\lambda_{max}(n \rightarrow \pi^*)$[c]		
No.	Diazene[a]	Dec pt,[b] °C	Uncoord	Coord	Proton nmr[d]
II	$(MeC_6H_4N{=}NC_6H_4Me)$	175	430	492	2.16 (d, 4), 3.00 (d, 4), 7.88 (s, 6), 9.0 (m, 30)
III	$(FC_6H_4N{=}NC_6H_4F)$	150	416	488	2.20 (d, 4), 3.22 (d, 4), 9.0 (m, 30)
IV	$(C_6H_5N{=}NC_6H_5)$	140	420	487	2.6 (m, 10), 9.0 (m, 30)
V	$(EtOC_6H_4N{=}NC_6H_4OEt)$	160	432	492	2.16 (d, 4), 3.16 (d, 4), 4.28 (q, 4), 8.84 (t), 9.0 (m, 36)
VI	$(H_2NC_6H_4N{=}NC_6H_4NH_2)$	125	432	480	2.32 (d, 4), 3.66 (d, 4), 7.32 (s, 4), 1.0 (m, 30)
VII	$(Me_2NC_6H_4N{=}NC_6H_4NMe_2)$	190	434		
VIII	$(3{,}5Me_2C_6H_3N{=}NC_6H_3Me_2)$	145			2.50 (s, 4), 3.40 (s, 2), 7.68 (s, 12), 1.0 (m, 30)

[a] The substituents on compounds II–VII are para. [b] There was considerable darkening below these temperatures. [c] Determined in toluene; units are nanometers. [d] Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Numbers in the parentheses are integrations.

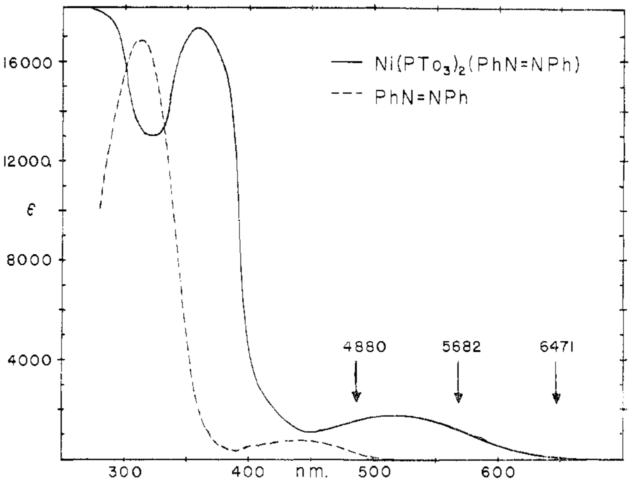


Figure 1. Electronic spectra of free azobenzene and $Ni(PTo_3)_2$-(PhN=NPh).

nitrobenzene (Stohler Isotope Chemicals) was converted to azobenzene using a scaled-down procedure based upon the method of Vogel.[28]

$Ni(COD)_2$ (0.373 g, 1.36 mmol), PTo_3 (0.826 g, 2.71 mmol), and ^{15}N-enriched azobenzene (0.25 g, 1.36 mmol) were allowed to react in pentane (8 ml). The material was filtered and washed with a small portion of cold pentane before drying under vacuum. After physical characterization was complete, the enriched azobenzene was recovered in 90% yield by slow air oxidation of the complex, followed by pentane extraction.

The unenriched complex was prepared on a larger scale in the same manner. The electronic spectrum is presented in Figure 1 together with the spectrum of uncoordinated azobenzene. The Raman spectra of the enriched and unenriched complexes were recorded in the solid state using a 647.1-nm exciting line and the spectrum of the unenriched complex was also recorded using a 568.2-nm exciting line. These spectra are shown in Figure 2 and peak positions are tabulated in Table III.[30] The background of the 568.2-nm spectrum was much higher than that observed at 647.1 nm. An attempt to record the spectrum using a 488.0-nm exciting line resulted in an extremely high background with no observable peaks. We noticed a green-brown band on the spinning sample which we initially attributed to decomposition of the compound in the laser beam. When the laser beam was turned off, the band faded within a matter of seconds. The appearance and disappearance of the band is reversible with laser light. It was ascertained that the band had not disappeared because of tumbling of the solid sample in the vertical tube.

Attempted Preparation of $Ni(PTo_3)_2$(*cis*-PhN=NPh). *cis*-Azobenzene was prepared by a literature method.[28] $Ni(COD)_2$ (0.52 g, 1.9 mmol) and PTo_3 (1.15 g, 3.8 mmol) were allowed to react in hexane to give a dark red suspension. A benzene solution of an excess of *cis*-azobenzene was injected dropwise into the stirred suspension. Each drop produced a momentary green-brown color which quickly changed to dark red. As soon as the addition was complete, the product was filtered and dried under vacuum. The reaction solvent was exposed to air and evaporated. Extraction as described for the ^{15}N-enriched sample resulted in the recovery of *trans*-azobenzene. The complex isolated was identical with the *trans*-azobenzene complex in all respects.

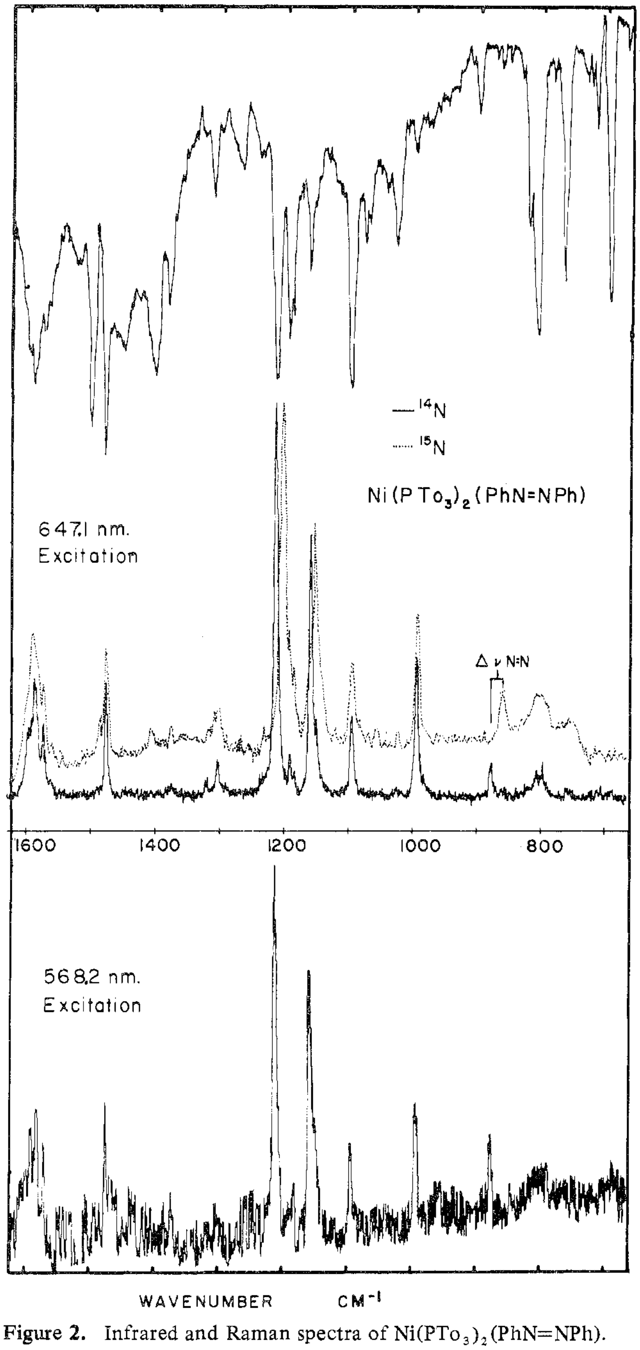


Figure 2. Infrared and Raman spectra of $Ni(PTo_3)_2$(PhN=NPh).

Preparation of $Ni(PTo_3)$(BC) (IX). $Ni(COD)_2$ (2.11 g, 7.68 mmol), PTo_3 (4.78 g, 15.4 mmol), and benzo[*c*]cinnoline (BC) (1.40 g, 7.68 mmol) were placed in a Schlenk flask under argon and hexane (20 ml) was injected. The mixture was stirred for 15 min and collected by vacuum filtration. The material was washed with a portion of cold hexane and recrystallized from toluene–hexane in a Dry Ice–acetone bath. The dark green-brown crystalline product melted with decomposition as high as 330° but the decomposition point was dependent on the rate at which the temperature was approached.

Attempted Hydrogenation of $Ni(PTo_3)_2(PhN{=}NPh)$. A portion of complex I was dissolved in benzene and hydrogen was bubbled through for 4 hr. There was no change in the sample nor was there when the procedure was repeated in the presence of 5% Pt on charcoal nor when the sample was stirred under 40 lb in.$^{-2}$ of hydrogen.

Attempted Protonation and Alkylation of $Ni(PTo_3)_2(PhN{=}NPh)$. Reaction of complex I in ether with trifluoroacetic acid resulted in a yellow oil which was identified as the tritolylphosphonium salt and free azobenzene. Similar results were obtained when the complex was allowed to react with trimethyloxonium tetrafluoroborate in ether.

Preparation of $Ni(PEt_3)_2(BC)_2$ (X). $Ni(COD)_2$ (1.05 g, 3.83 mmol) and benzo[*c*]cinnoline (0.70 g, 3.83 mmol) were placed under argon and hexane was injected. PEt_3 (0.92 g, 7.66 mmol) was injected and the stirred mixture immediately darkened. A highly crystalline black product precipitated in a few minutes and was collected by vacuum filtration; mp 330°. Integration of the nmr spectrum indicated one BC per one PEt_3: 3.0 (m, 16), 9.0 (m, 30).

Preparation of $Ni(PPh_3)_2(AIBN)$ (XI). $Ni(COD)_2$ (3.32 g, 12.1 mmol), PPh_3 (6.33 g, 24.1 mmol), and azobis(isobutyronitrile) (AIBN) (1.98 g, 12.1 mmol) were placed in a Schlenk flask and pentane was injected. The suspension immediately turned red and then purple. Filtration yielded an unstable, pyrophoric material which decomposed slowly on standing in the solid state or quickly in solution. The infrared spectrum contained a weak $C{\equiv}N$ stretch at 2178 cm^{-1}. Chemical analysis and nmr characterization were impossible because of the instability of the compound. Preparation of the complex and then rapid addition of an excess of PPh_3 resulted in formation of $Ni(PPh_3)_4$ and recovery of some of the starting AIBN.

Decomposition of $Ni(PPh_3)_2(AIBN)$. Stirring the AIBN complex for several minutes at 0° in benzene resulted in the loss of 1 equiv of dinitrogen and formation of a very insoluble, golden orange microcrystalline compound (XII) which had $\nu(C{\equiv}N)$ at 2130 cm^{-1} (weak). Attempted preparation of the previous AIBN complex in benzene resulted in this product. The compound analyzes as $Ni(PPh_3)_2(C_8H_{12}N_2)$. Stirring of the compound with an excess of PPh_3 or tetracyanoethylene in toluene or pentane resulted in no reaction. Exposure of the solid compound to air resulted in charring, but exposure to air while the compound was stirred in suspension in a variety of solvents resulted in formation of acetone and $Ni(PPh_3)_2(CN)_2$ (characterized by comparison with an authentic sample ($\nu(C{\equiv}N)$ 2110 cm^{-1})).

Attempted Preparation of $Ni(PEt_3)_2(AIBN)$. This synthesis was attempted using the same procedure as for the PPh_3 analog. There was an initial dark red-purple product which quickly lightened to yellow. The only product isolated was $Ni(PEt_3)_2(CN)_2$.

Preparation of $[Ni(pyN{=}Npy)]_n$ (XIII). $Ni(COD)_2$ (0.42 g, 1.52 mmol) and azopyridine (0.28 g, 1.52 mmol) were dissolved in separate 10-ml portions of toluene and the two solutions were combined slowly with stirring. Reaction was quantitative, yielding a very dark red-brown polymeric material insoluble in common organic solvents; dec pt >360°. Ir: 1600 (s), 1540 (m), 1465 (s), 1442 (s), 1380 (w), 1367 (w), 1335 (w), 1294 (m), 1265 (w), 1232 (m), 1210 (w), 1157 (m), 1118 (w), 1064 (m), 1002 (m), 950 (w), 855 (w) cm^{-1}.

Attempted Preparation of $Ni(PEt_3)_2(pyN{=}Npy)$. In an attempt to prepare a π-type complex, $Ni(COD)_2$ (1.37 g, 4.98 mmol) and PEt_3 (1.18 g, 9.96 mmol) were allowed to react in ether, and an ether solution of azopyridine (0.92 g, 4.98 mmol) was added. The dark red mixture quickly turned brown and the triethylphosphine was carried through in solution when the mixture was filtered, leaving a residue of the polymeric material described in the preceding synthesis.

Attempted Preparation of $Ni(PPh_3)_2(NCN{=}NCN)$. $Ni(COD)_2$ (0.33 g, 1.2 mmol) and PPh_3 (0.66 g, 2.5 mmol) were allowed to react in benzene (15 ml) and a benzene solution of DCND (0.10 g, 1.2 mmol) was added dropwise with stirring. The red suspension turned yellow and the only product isolated was identified as $Ni(PPh_3)_2(CN)_2$ by comparison with an authentic sample. Analogous results were obtained using PTo_3 and PEt_3.

Attempted Preparation of $Ni(PPh_3)_2(MeC_6H_4N{=}NCN)$. $Ni(COD)_2$ (0.50 g, 1.8 mmol) and PPh_3 (1.0 g, 3.7 mmol) were allowed to react in diethyl ether (15 ml) and an ether solution of an excess of the diazene was added with stirring. An orange oil formed and the only product isolated, in low yield, was again $Ni(PPh_3)_2(CN)_2$.

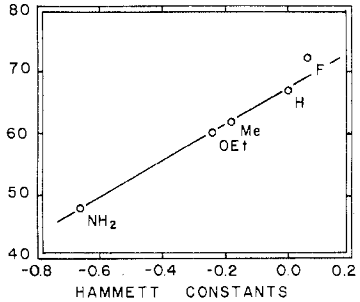


Figure 3. Plot of the changes in n → π^* *vs.* the Hammett σ parameters for a series of bis(triethylphosphine)nickel(0) complexes of para-substituted azobenzenes.

Preparation of $Ni(PTo_3)_2(ToCONNCOTo)$ (XIV). $Ni(COD)_2$ (2.20 g, 8.0 mmol) was allowed to react with PTo_3 (4.86 g, 16.0 mmol) and bis(*p*-methylbenzoyl)diazene, ToCONNCOTo (2.13 g, 8.0 mmol), in hexane (20 ml). The mixture turned red initially and then a yellow precipitate formed. The yellow precipitate had an infrared spectrum almost identical with the platinum analog (which was prepared by the method of Kasenally[24]). In a variety of solvents the yellow compound gave red or brown solutions from which the yellow material was not recovered.

Discussion

Spectral and Stability Trends of Complexes of Para-Substituted Azobenzenes. The series $Ni(PEt_3)_2(XC_6H_4N{=}NC_6H_4X)$, where the X are para substituents, was chosen for spectral study because it was observed that the band assignable to the n → π^* transition of the azobenzene in triethylphosphine complexes is not a shoulder, as is the case in complexes of some of the other phosphines,[6] but is distinct and therefore its position can be determined with relatively more accuracy. There is no obvious trend in the n → π^* transitions listed in Table I, but we find a correlation between the change in the position of the absorption upon coordination and the Hammett constants (σ—para) for the substituents. This correlation, displayed in Figure 3, indicates that the more electron-withdrawing substituents cause greater differences between the coordinated and uncoordinated values. We have already demonstrated that the absorption is shifted to higher energy as electron density on the N=N double bond of a given azobenzene is increased by introduction of more basic ligands to the complex.[6] In the present PEt_3 series, the electron density on the azobenzene is being altered by changing the ring substituents. The present data indicate, as expected, that the change in the electron density on the nitrogen atoms may be affected by the phenyl substituents as well as by the trans ligands. The relationship between the strength of the metal–azobenzene bond and the n → π^* transition in the two series of compounds is different. In the previously reported series where the phosphines were varied but the diazene was held constant it was shown that shifts to higher energy indicate that the azobenzene is coordinated more strongly. The opposite effect is observed when varying the azobenzene and holding the ligand constant. There is extensive dissociation of the azobenzene complexes with electron-donating substituents; the N=N bond is not able to undergo π back-bonding as readily and therefore the complex is less stable. This would not be predicted from a consideration of only the n → π^* transitions of the uncoordinated azobenzenes. Normally it would be assumed that the molecule with the smallest energy between its highest occupied molecular orbital and its lowest unoccupied molecular orbital would be most likely to form strong bonds. In this case it is apparent that there are other effects which are more important than the energy of the lowest transition.

The trend in the stabilities of the complexes is that expected from a consideration of the electron-donating or -withdrawing abilities of the substituents. The effect of the substituent is transmitted through the ring to the N=N bridge where it has a pronounced effect on the bonding of the azobenzene to the nickel atom. It becomes clear that the amount of back-bonding to the azobenzene determines the strength of the metal–azo bond but this back-bonded electron density is not necessarily localized on the N═N bond. It can be delocalized to the phenyl rings and their substituents. While complexation puts electron density into the π^* orbitals of the diazene, electron-withdrawing substituents on the phenyl rings remove it. It would be predicted that a structure of a nickel azobenzene complex with electron-withdrawing substituents on the azobenzene would have a shorter nickel–nitrogen distance, in accord with the Dewar–Chatt–Duncanson model for π bonding. However, the N═N bond might not be lengthened as much as would be predicted because of the π^* delocalization. Baraban and McGinnety[31] have concluded that the Dewar–Chatt–Duncanson model does not provide a good description of the bonding in $Pt(CF_3CFCFCF_3)(P(C_6H_5)_3)_2$, where there are also electron-withdrawing substituents on the unsaturated ligand.

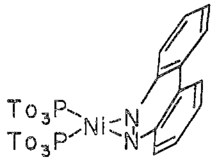
Spectroscopy of $Ni(PTo_3)_2(PhN{=}NPh)$ (I). We noted earlier[9] that in σ-bonded aryldiazene complexes the N═N stretching vibration is often not observed in the infrared spectrum but is the strongest band in the Raman spectrum. For the symmetrically bound azobenzene complex, several bands in the infrared spectrum (Figure 2 and Table III[30]) shift small amounts upon ^{15}N substitution but none by the amount expected for disubstitution. In the Raman spectrum recorded using a 647.1-nm exciting line (Figure 2 and Table III[30]) small isotopic shifts are observed for the strong peaks (1215→1202, 1160→1154 cm^{-1}), and the small peak at 876 cm^{-1} shifts by 21 cm^{-1}, an amount expected for disubstitution of a three-membered ring. Though this band may contain a significant portion of N═N stretching mode character, the three-membered ring would not be expected to give a pure N═N stretching vibration, but rather a ring deformation. This band is too low in frequency to be compared with the band around 1500 cm^{-1}, which has been observed in a variety of olefin complexes[32] and attributed to ν(C═C). Olefin complexes display a lower frequency band around 1250 cm^{-1} which might contain a greater contribution from the C═C stretching mode than does the higher frequency band. The stretching frequency ν(C═C) in free ethylene is observed at 1623 cm^{-1} and the shift to the lower band at 1245 cm^{-1} in a Ni(0) complex[32b] is 378 cm^{-1}. In free azobenzene ν(N═N) is observed at 1440 cm^{-1} and hence there is a shift of almost 600 cm^{-1} in this complex.[33] This greater shift is consistent with the observation[8] that azobenzene π back-bonds better than do unactivated olefins. However, on the basis of the isotopic shifts of the 1215-, 1160-, and 876-cm^{-1} bands on substitution of ^{15}N it is probable that here again extensive coupling of bands with and without intrinsic intensity is occurring. As has been shown by more extensive substitution experiments for various diazene complexes, these spectra are more complicated than might be expected initially.[34]

The position of the 647.1-nm exciting line relative to the position of the n → π^* transition in the electronic spectrum is shown in Figure 1. When the line at 568.2 nm, which is partially absorbed by the n → π^* band, is used as an exciting line, the background for the spectrum is much higher, but it can be seen that the peak at 876 cm^{-1} is now stronger relative to other peaks around it. This effect, though not very pronounced, is reproducible and may be attributed to preresonance enhancement. This is not the very marked resonance Raman effect which has been observed in some inorganic systems[35] but is comparable to effects which have been observed in other azo systems.[33] The enhancement of a band which may contain a reasonable amount of N═N stretching character supports the assignment of the n → π^* transition which would be centered on the N═N bond.

When the experiment is repeated using the 488.0-nm exciting line no spectrum is observed above the extremely high background, and the sample changes from its normal violet to a green-brown color. The reversibility of the color change over a short period of time suggests two possible stereochemical mechanisms. The first is a trans → cis isomerization of the coordinated azobenzene; the second is a change in the mode of coordination of the azobenzene from a symmetrical π bond to an unsymmetrical σ bond through one of the nitrogen lone pairs.

The first mechanism is supported by a number of observations. Photochromism has been observed in a variety of azo compounds[15] and has been shown to result from a photochemical trans → cis isomerization which thermally reverts back to the trans species. When the synthesis of the *cis*-azobenzene complex is attempted, there is a momentary green-brown species very similar in color to the species observed in the Raman experiment. The species isolated is the violet, isomerized trans complex. Since the cis → trans isomerization of azobenzene requires days to go to completion, the rapid conversion observed here is catalyzed by the nickel(0) species present.[36]

In an attempt to prevent the cis → trans isomerization of coordinated azobenzene, the analogous benzo[*c*]cinnoline complex was prepared. This *cis*-azobenzene has the two rings joined at the ortho position. It has been shown to coordinate in a bridging manner in several complexes.[37] In the present Ni(0) system the resulting π complex, IX, is brown but when viewed against a violet background it has the green-brown color observed in the laser experiment. It thus appears that the trans → cis → trans isomerization process is a reasonable explanation for the observations. However, there is some support for the second mechanism. When one attempts to prepare the same benzo[*c*]cinnoline complex with triethylphosphine in place of triarylphosphines, the only species isolated from the reaction mixture is unlike any of the previous complexes. Instead of the red, purple, or brown of the compounds isolated earlier, the triethylphosphine complex precipitates as black crystals which when dissolved in benzene yield intensely colored brown solutions. The compound, X, analyzes for two phosphine and two benzo[*c*]cinnoline (BC) molecules. It may be that the BC is not π bonded but is unsymmetrically σ bonded through nitrogen lone pairs. It would be reasonable to assume that the complex has a four-coordinate structure with two phosphorus atoms and two nitrogen atoms coordinated to the nickel atom, but support for this model must await an X-ray structure determination as the nmr and infrared spectra do not yield to ready interpretation. If this model is correct, then it may be that the photochromic process is one in which the *trans*-azobenzene shifts from a π bond to a σ bond and then back to a π bond.



IX

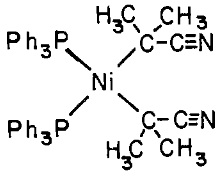
Chemical Inertness of $Ni(PTo_3)_2(PhN{=}NPh)$. Since there is a higher degree of π back-bonding to azobenzene in its complexes than there is to stilbene in the isoelectronic olefin complex,[8] we felt that the coordinated azobenzene might react with electrophilic reagents. Unfortunately, this does not seem to be the case. Reaction of the complex with trifluoroacetic acid, trimethyloxonium tetrafluoroborate, or methyl(trifluoromethyl)sulfonate yields free azobenzene, the respective phosphonium salts, and other uncharacterized material. It is not known if the initial attack takes place at the nitrogen atoms, but as the complex falls apart, the phosphines are much more likely to undergo protonation or methylation.

It has been shown that coordinated aryldiazenes can be hydrogenated under mild conditions to yield complexes of arylhydrazines.[38] In addition, it has been shown that coordinated azobenzene can be reduced under mild conditions to yield uncoordinated 1,2-diphenylhydrazine.[2] All attempts to hydrogenate the present azobenzene complex failed. Even at elevated pressures of hydrogen in the presence of catalyst, there was no apparent change in the complex. Starting materials were recovered in high yield.

Reaction of Azobis(isobutyronitrile) (AIBN) with Nickel(0). The reaction of triphenylphosphine and AIBN with nickel(0) leads to a pyrophoric, highly unstable compound (XI). The large shift in the $C\equiv N$ stretching frequency (from 2250 cm^{-1} for free AIBN to 2178 cm^{-1} for coordinated AIBN) indicates that there is an interaction between the nitrile group and the metal. The fact that the AIBN can be displaced from the complex implies that it is still intact, and one $C\equiv N$ stretching frequency implies that the two nitriles are equivalent. There is a possibility that the molecule is π bonded through the nitrogen atoms of the diazene bridge. There is no band in the spectrum which can be assigned to the $N{=}N$ stretching frequency which, based upon the azobenzene complexes, would be expected to decrease markedly. The $C\equiv N$ stretching frequency might decrease, but in Ni(0) complexes of cyanoolefins where the nitrile groups are conjugated with the double bond, the changes in the $C\equiv N$ stretching frequencies are only 50 cm^{-1}.[32,39] Because the nitrile is not conjugated with the diazene double bond we expect that the change in the $C\equiv N$ stretching frequency should be less in this system. If the molecule were π bonded through the nitriles, one would expect a decrease of 200–250 cm^{-1} in the $C\equiv N$ stretching frequency,[40] so this model should be ruled out. Finally, there is the possibility of coordination through the lone-pair electrons on the nitrogen atom of the nitrile. Though this type of coordination commonly raises the $C\equiv N$ stretching frequency,[41a] it has been shown[41b] that electron-rich metals can cause a decrease in the frequency. In the complex $Ni(PPh_3)_3(C_6H_5CN)$, the $C\equiv N$ stretching frequency decreases 72 cm^{-1} [41c] relative to C_6H_5CN. Therefore we assume nitrile coordination in the present complex.

When XI is dissolved, dinitrogen is evolved as the coordinated AIBN decomposes. The stability of XI in the solid state compared with the rapid decomposition in solution implies that the complex is stabilized by solid-state effects. The only reason that it was observed was that the reaction was run initially in a solvent in which the product is very insoluble. The fact that the PEt_3 complex would be more soluble, even in hexane, might explain the fact that an initial AIBN complex could not be isolated from that reaction.

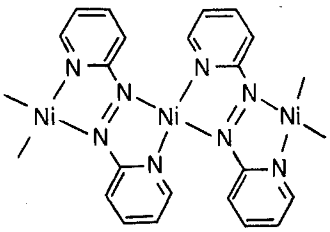
The rapid decomposition of the coordinated AIBN and evolution of dinitrogen can be attributed to a lowering of the barrier to trans → cis isomerization. We have shown that the cis → trans isomerization of azobenzene takes place much faster in the presence of Ni(0). This lowering of the activation energy must also make the reverse process easier. Isomerization of the AIBN to the cis species, which is less stable, leads to the evolution of dinitrogen and the formation of two cyanoisopropyl groups to yield a golden, slightly air sensitive, polycrystalline nickel(II) dialkyl complex, XII. This is supported by a number of observations.



XII

The product normally formed in highest yield in the decomposition of AIBN is tetramethylsuccinonitrile.[12] This molecule could coordinate to the nickel atom through its nitrogen lone pairs but this would lead to a $C\equiv N$ stretching frequency higher than the 2130 cm^{-1} observed. The decomposition of free AIBN is also known to lead to a substituted ketenimine. A complex of this species would be similar in nature to a ketenimine complex formed by the nickel(0) -catalyzed reaction of dicyanodiazomethane with coordinated *tert*-butyl isocyanide.[42] This type of π-bonded complex must be ruled out, however, by the fact that the coordinated species could not be displaced from the complex by an excess of phosphine or tetracyanoethylene. This indicates that XII is nickel(II) σ bonded to alkyl groups. The formation of acetone during the air oxidation of XII indicates that there are cyanoisopropyl groups present in the complex. Attack by oxygen on the complex results in cyano migration to the metal and evolution of acetone.

(2,2'-Azopyridine)nickel(0) (XIII). In the course of our investigation of aromatic diazene systems we prepared 2,2'-azopyridine. This interesting molecule has the ability to coordinate in a variety of fashions involving the nitrogen atoms of both the pyridines and the diazene bridge[17] and it seemed unlikely that it would utilize only the diazene bridge. The only species which could be isolated under a variety of conditions was a highly insoluble material, XIII, which analyzes for one azopyridine for each nickel. Assignment of a structure on the basis of the infrared spectrum is simplified by the absence of any ligands other than the azopyridine. The spectrum, which is similar to that of the free ligand, is characterized by skeletal frequencies. Using the notation of Baldwin, *et al.*,[17] the four important bands are as follows: band I, 1600 cm^{-1}; band II, 1540 cm^{-1}; band III, 1465 cm^{-1}; band IV, 1442 cm^{-1}. These band positions are indicative of a very symmetrical mode of coordination involving all four nitrogen atoms. We thus suggest a polymeric structure such as involving bridging azopyridines (the figure is not meant to imply square-planar coordination). Such a structure is consistent with the low $N{=}N$ stretching frequency at 1380 cm^{-1} and the ring breathing mode at 1002 cm^{-1}, if one assumes considerable π delocalization. Although it has been shown that π back-bonding is unimportant in platinum(II) σ-bonded diazene complexes,[9,43] this system demonstrates that for a metal in a low oxidation state, the electron density on the metal can be delocalized through π back-bonding to a σ-bonded diazene.



XIII

Reaction of Cyanodiazenes with Nickel(0). The reaction of dicyanodiazene (DCND) with $IrCl(CO)(PPh_3)_2$ has been shown to yield two products, both of which contain intact DCND molecules.[22] By combining stoichiometric quantities of DCND and $IrCl(CO)(PPh_3)_2$ a 1:1 complex is formed. By addition of an excess of DCND, a 2:1 complex is formed. Both of these complexes are presumed to contain DCND π bonded in a manner analogous to the bonding of TCNE.[23]

When DCND is allowed to react with nickel(0), no such adduct is formed. Rather, a dicyanonickel(II) species is formed with evolution of dinitrogen. When the reaction is attempted

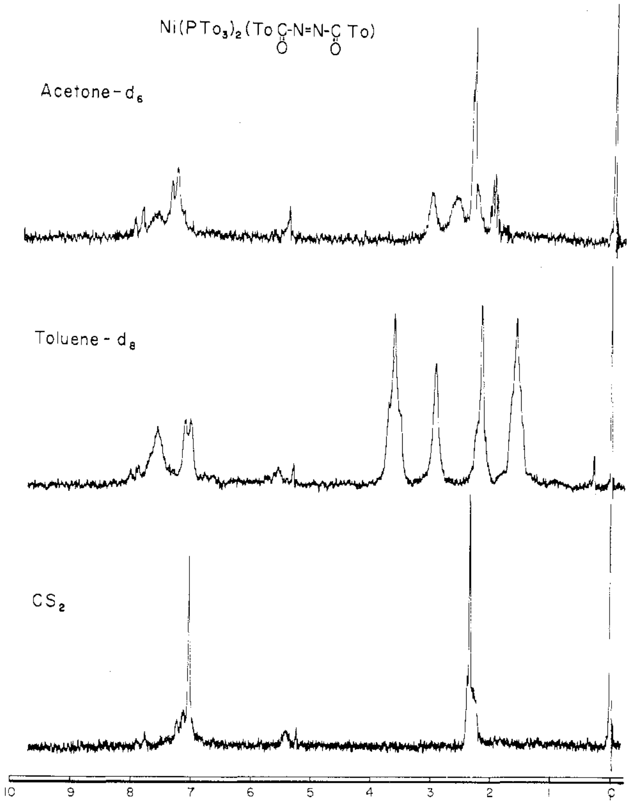
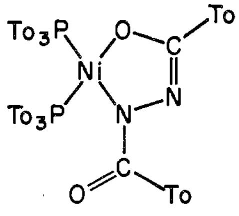


Figure 4. Proton nmr spectrum of (bis(*p*-methylbenzoyl)hydrazido)bis(tri-*p*-tolylphosphine)nickel(II) recorded at 34° in acetone, toluene, and carbon disulfide.

with tolylcyanodiazene, the same product is formed but in much lower yield. Thus we again find that nickel(0) catalyzes the decomposition of a substituted diazene to yield dinitrogen and an oxidized nickel species. The greater stability of Ir(I) compared with Ni(0) may explain the difference in their reactions with DCND.

Reaction of Bis(*p*-methylbenzoyl)diazene with Nickel(0). The infrared spectrum of the yellow complex formed by the reaction of nickel(0), tri-*p*-tolylphosphine, and bis(*p*-methylbenzoyl)diazene is almost identical with the spectrum of the tolyl analog of (dibenzoylhydrazido)bis(triphenylphosphine)platinum(II). Since the structure of the platinum species is known,[7] we assumed that the nickel complex (XIV)



XIV

is similar in nature.

To confirm the unsymmetrical mode of bonding, the nmr spectrum was recorded. Solutions were not the expected yellow but were brown. The nmr spectrum recorded for a C_6D_6 solution seemed at first to be totally unreasonable. The spectrum rerecorded for a toluene-d_8 solution is different, but integration of both spectra indicated a ratio of alkyl to aryl protons much higher in alkyl than the 3:4 expected for tolyl groups. Spectra were then recorded for the complex dissolved in a variety of solvents. Some of these spectra are shown in Figure 4.

The unusual solvent dependence of the nmr spectra is readily explicable as an equilibrium between a square-planar, diamagnetic species and a tetrahedral, paramagnetic species. It is well established that nickel(II) species can exist in the two isomeric forms.[44] The equilibrium has been studied by nmr in a variety of systems.[45-47] Complexes of dihalobis(trialkylphosphines) are red, diamagnetic, square-planar species and those of triarylphosphines are green or brown, paramagnetic, tetrahedral species. It was found that by using alkyldiarylphosphines and careful control of conditions several compounds could be crystallized in either the red or green forms. The square-planar species were favored by nonpolar solvents and low temperature while the tetrahedral species were favored by polar solvents and higher temperatues.

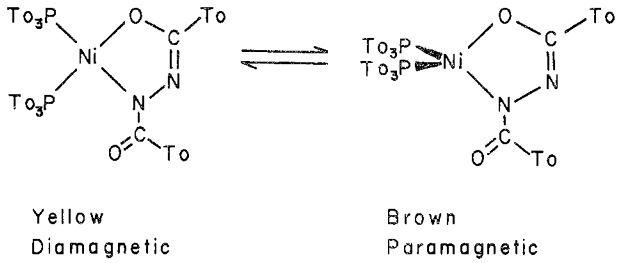


Figure 5. Dynamic equilibrium between the square-planar and tetrahedral isomers of (bis(*p*-methylbenzoyl)hydrazido)bis(tri-*p*-tolylphosphine)nickel(II).

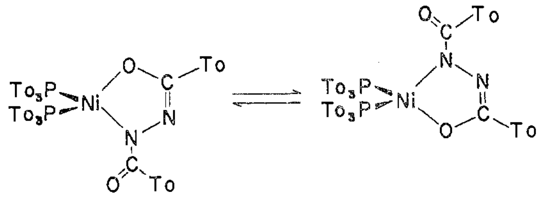


Figure 6. Proposed dynamical process which makes the two tolyl groups of the diazene equivalent on the nmr time scale.

In the present system, the equilibrium, shown in Figure 5, shows the same type of solvent dependence found in the nickel(II) halide systems. Carbon disulfide shifts the equilibrium toward the diamagnetic species resulting in a simple spectrum. Aromatic solvents result in a more complex spectrum, as does acetone. The interconversion is found to be rapid on the nmr time scale. Therefore, the spectrum is a weighted average of the diamagnetic and isotropically shifted paramagnetic resonances. We found that at elevated temperatures there is a second dynamical process shown in Figure 6 which makes the two tolyl groups of the diazene equivalent. More detailed nmr results on this dynamical system and other closely related systems will be reported elsewhere.

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Registry No. I, 51139-65-2; I($^{15}N_2$), 54353-08-1; II, 54325-33-6; III, 54325-34-7; IV, 54325-35-8; V, 54325-36-9; VI, 54325-37-0; VII, 54325-38-1; VIII, 54307-55-0; IX, 54307-56-1; X, 54307-66-3; XI, 54340-40-8; XII, 54307-57-2; XIII, 54307-59-4; XIV(sq. planar), 54307-60-7; XIV(tetrahedral), 54352-34-0; $Ni(COD)_2$, 1295-35-8.

Supplementary Material Available. Table II listing the analytical data and Table III listing spectroscopic data 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, 24× 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 $2.50 for microfiche, referring to code number AIC40580N.

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(29) Abbreviations used throughout the paper are Ph = phenyl, To = *p*-tolyl, Xy = 3,5-xylyl, Me = methyl, Et = ethyl, COD = 1,5-cyclooctadiene, BC = benzo[*c*]cinnoline, AIBN = azobis(isobutyronitrile), py = pyridyl, and DCND = dicyanodiazene.

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Role of Cationic Trans Intermediates in Promoting the Insertion of Unsaturated Hydrocarbons into Platinum–Hydrogen and Platinum–Carbon Bonds. A Study of the Insertion Reaction Involving Compounds of the Type *trans*-$[PtMe(\eta^2\text{-}C_3H_4)(PMe_2Ph)_2]^+Z^-$

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The insertion reaction of methylplatinum complexes *trans*-$[PtMe(\pi\text{-allene})(PMe_2Ph)_2]^+Z^-$, to *cis*-$[Pt(\pi\text{-2-methylallyl})(PMe_2Ph)_2]^+Z^-$, where $Z^- = BF_4^-$, PF_6^-, and SbF_6^-, has been studied in the temperature range 0–40° in CH_2Cl_2, CD_2Cl_2, $CHCl_3$, and $CDCl_3$. The reaction is first order in *trans*-$[PtMe(\pi\text{-allene})(PMe_2Ph)_2]^+Z^-$ and shows an anion dependence in the thermodynamic properties (ΔH^*) of the activated complex: $SbF_6^- \sim BF_4^- > PF_6^-$. The addition of the neutral donor or anionic ligands I^-, NO_3^-, pyridine, CO, and PPh_3 leads to displacement of the π-bonded allene ligand: no insertion occurs. Addition of allene leads to rapid exchange of free and coordinated allene on the nmr time scale and suppresses the overall rate of insertion. General schemes for Pt–H and Pt–C insertion reactions based on (i) five-coordinate intermediates and (ii) four-coordinate intermediates are discussed. The importance of coordination to an electrophilic metal center is stressed if Pt–H and Pt–C insertion reactions are to be favored.

Initial coordination of an unsaturated molecule followed by insertion into a metal–hydrogen or metal–carbon bond is believed[1] to form the basis for most metal-catalyzed reactions of unsaturated hydrocarbons. In the field of d^8 transition metal chemistry five-coordinate π complexes of type I have often been invoked[2] as the reactive intermediates in insertion reactions of type (1). Consistent with this proposal was the finding by Clark and Puddephatt[3] that hexafluorobut-2-yne, $CF_3C{\equiv}CCF_3$, reacted with *trans*-$PtCl(Me)(AsMe_2Ph)_2$ to give the insertion product *trans*-$PtCl(CCF_3{=}C(CH_3)CF_3)(AsMe_2Ph)_2$