Journal of Organometallic Chemistry, 74 (1974) 121—134

NICKEL(0) STILBENE COMPLEXES AND THE STRUCTURE OF BIS(TRI-*p*-TOLYLPHOSPHINE)(*trans*-STILBENE)NICKEL(0) HEMITETRAHYDROFURANATE

STEVEN D. ITTEL and JAMES A. IBERS

Department of Chemistry, Northwestern University, Evanston, Illinois 60201 (U.S.A.)

(Received December 21st, 1973)

Summary

A series of nickel(0)—stilbene complexes has been prepared by the reaction of triarylphosphines or tert-butyl isocyanide with bis(1,5-cyclooctadiene)nickel(0) in hexane. The structure of the complex bis(tri-*p*-tolylphosphine)(*trans*-stilbene)-nickel(0) hemitetrahydrofuranate, $Ni[P(C_6H_4CH_3)_3]_2[(C_6H_5)HC{=}CH(C_6H_5)] \cdot 0.5(C_4H_8O)$, has been determined at room temperature from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final R index (on F) of 0.092 based on 2417 observations above background. The material crystallizes in the orthorhombic space group D_{2h}^{10}-*Pccn*, with eight molecules of complex and four molecules of solvent in a cell of dimensions $a = 19.548(8)$, $b = 26.145(12)$, $c = 19.718(9)$ Å. The Ni atom has trigonal coordination if the olefin is regarded as a monodentate ligand. The five atoms of the inner coordination sphere are distorted planar and the two olefinic carbon atoms are essentially equidistant from the nickel atom. The structure is compared with that of bis(tri-*p*-tolylphosphine)(azobenzene)nickel(0) determined previously. Observed differences in the bonding of the olefin and the isoelectronic azo complex are discussed.

Introduction

Although the bonding of unsaturated molecules to transition metals is of obvious interest in view of the importance of such metals in catalysis, the structural systematics even on simple olefin complexes are far from plentiful. Some systematics are beginning to emerge in studies of the system $NiL_2(Un)$, where L are phosphines or tert-butylisocyanide and Un is one of a variety of unsaturated molecules. The systems studied structurally to date include: L = t-BuN≡C, Un = diphenylacetylene [1], azobenzene [2], and tetracyanoethylene [3]; L = $PTol_3$ (Tol = *p*-tolyl), Un = azobenzene [4]; and L = PPh_3, Un = ethylene [5]. As part of a continuing series of chemical and structural studies in this area, the present paper reports the preparation and characterization of some Ni^0 stilbene complexes and the structure of the complex L = $PTol_3$, Un = *trans*-stilbene (1,2-diphenylethylene). Although a complex of *cis*-stilbene would be useful for comparison with the diphenylacetylene complex, complexes of *trans*-stilbene produced better crystals. The *trans*-stilbene complexes are of obvious use for comparison with the corresponding azobenzene complexes (hereafter referred to as the azo structure or complex). Although the complex L = t-BuN≡C, Un = *trans*-stilbene was most desirable for such a comparison, crystals of the material were unstable. Accordingly a structure determination has been carried out on L = $PTol_3$, Un = *trans*-stilbene, and the results are presented here.

Experimental

Preparation

The phosphines and stilbenes were obtained commercially and used as received. Bis(1,5-cyclooctadiene)nickel, $Ni(COD)_2$ [6] and tert-butylisocyanide [7] were prepared by standard methods. All solvents were free of oxygen and water and all reactions were carried out under an atmosphere of argon. All reactions were carried out at 0° with reaction times ranging from 10 to 30 min. Hydrocarbon mull infrared spectra were recorded on a Beckman IR-9 spectrometer and electronic spectra were recorded on a Cary 14 spectrophotometer. Melting points were determined in sealed evacuated capillaries and are uncorrected.

$Ni[(CH_3)_3CN{\equiv}C]_2$*(trans-stilbene)*

A hexane suspension of $Ni(COD)_2$ (1 g, 3.6 mmoles) was treated with t-BuN≡C (0.61 g, 7.3 mmoles) and *trans*-stilbene (0.67 g, 3.7 mmoles), to give the desired complex in high yield. The deep red, pyrophoric material was recrystallized from tetrahydrofuran as large red prisms which in the absence of solvent spontaneously lose THF of crystallization causing the crystals to powder. $\nu(N{\equiv}C)$ 2100, 2057 cm^{-1}; m.p. 105—107°. Found: C, 70.8; H, 7.6; N, 6.7. $NiN_2C_{24}H_{30}$ calcd.: C, 71.1; H, 7.5: N, 5.9%.

$Ni[(CH_3)_3CN{\equiv}C]_2$*(cis-stilbene)*

This moderately air-sensitive compound was prepared in a manner similar to that of the *trans* complex. The orange-red powder is easily converted to the *trans* complex by addition of *trans*-stilbene. On standing in solution, the complex decomposes to $[Ni(t\text{-}BuN{\equiv}C)_2]_n$ liberating the stilbene. Small quantities of *trans*-stilbene were isolated from reaction mixtures. $\nu(N{\equiv}C)$ 2080 cm^{-1}; m.p. 153—156° (dec.). Found: C, 70.6; H, 7.7; N, 7.2. $NiN_2C_{24}H_{30}$ calcd.: C, 71.1; H, 7.5; N, 6.9%.

$Ni[P(C_6H_5)_3]_2$*(trans-stilbene)*

A hexane suspension of $Ni(COD)_2$ (1 g, 3.6 mmoles) was treated with triphenylphosphine (1.91 g, 7.3 mmoles) and *trans*-stilbene (0.66 g, 3.7 mmoles). The dark red product, formed in high yield, was moderately air sensitive. M.p. 205—208° (dec.). Found: C, 78.5; H, 5.5. $NiP_2C_{50}H_{42}$ calcd.: C, 78.6; H, 5.6%.

Ni[P($C_6H_4CH_3$)$_3$]$_2$(trans-stilbene)

This dark red, moderately air-sensitive compound was prepared in the same manner as its triphenylphosphine analogue. M.p. 140—143° (dec.). Found: C, 79.5; H, 6.4. $NiP_2C_{56}H_{54}$ calcd.: C, 79.4; H, 6.4%.

Ni[P($C_6H_4CH_3$)$_3$]$_2$(cis-stilbene)

Attempts to prepare this compound in a pure form using the methods described previously were unsuccessful because of an unfavorable equilibrium between the desired red complex and the yellow $Ni[P(C_6H_4CH_3)_3]_2$(COD). Repeated isolation of the mixed products in the presence of an excess of the *cis*-stilbene led to the desired product in states of varying purity as indicated by integration of the NMR spectra.

Ni[P($C_6H_4CH_3$)$_3$]$_2$(trans-azobenzene)

This product, reported previously [4], may be prepared in high yield by reaction of stoichiometric quantities of the *trans*-stilbene complex and azobenzene. λ_{max} (ϵ) 523 (1760); 355 (19200); 280 nm (sh) (20100).

Crystallographic data

$Ni(PTol_3)_2(PhHC{=}CPhH) \cdot 0.5C_4H_8O$; crystallized from cyclohexane/benzene/THF, 1/2/2; orthorhombic, a = 19.548(8), b = 26.145(12), c = 19.718(9) Å, V = 10078 Å^3, d_{calc} = 1.16 g cm^{-3} for Z = 8. Linear absorption coefficient for Cu-K_α radiation 13.9 cm^{-1}. The air sensitivity of the compound precluded an experimental determination of the density.

Precession and Weissenberg photographs of zero, first, and second level zones taken with Cu-K_α radiation showed systematic absences of $0kl$ reflections when $l \neq 2n$, $h0l$ reflections when $l \neq 2n$, and $hk0$ reflections when $h + k \neq 2n$. These absences are characteristic of the orthorhombic space group D_{2h}^{10}-*Pccn*.

Intensity measurements were made at 23° with a computer-controlled Picker Four Circle Diffractometer using Cu-K_α radiation prefiltered with 0.5 mil Ni foil. The crystal, which had the approximate dimensions in x, y and z of 0.2, 0.2 and 0.7 mm, was sealed in an argon-filled quartz capillary. The setting angles of twelve reflections were determined using a narrow vertical slit at a take-off angle of 1°. Cell parameters and crystal orientation were then derived by a least-squares procedure. The take-off angle for data collection was 3.6°. The counter was positioned 23 cm from the crystal and was preceded by an aperture of dimensions 6 × 6 mm. The pulse height analyzer was set to admit 90% of the Cu-K_α peak and copper foil attenuators were automatically inserted if the intensity of the diffracted beam exceeded about 7000 cps during the scan. Peaks were scanned using the θ—2θ technique starting 0.9° before the K_{α_1} peak and ending 0.9° after the K_{α_2} peak. All reflections were scanned at 2° per minute and background counts were taken at each end of the scan range. The background counts were for 10 sec out to 2θ = 49°, 20 sec from 2θ = 49 to 75°, and 40 sec for the remainder out to 2θ = 80°. Data collection was terminated at this point because the last shell yielded relatively few intensities above background.

The intensities of six standard reflections were measured every 100 reflections. The standard deviations of these reflections, computed on the basis of the agreement among the 38 observations made for each standard, were at the most little more than twice the deviations based on counting statistics alone. There was no trend in the variations.

All data were processed as described previously [8]. A value of 0.04 was used for p in the estimation of $\sigma(F_o^2)$. Of the 3468 observed reflections 2420 obeyed the conditions $F_o^2 > 3\sigma(F_o^2)$ and only these reflections were used in the subsequent calculations. A narrow range of transmission coefficients (0.78—0.82) was determined in trial calculations and so no absorption correction was applied.

Structure solution and refinement

The structure was solved using symbolic addition in combination with least-squares and Fourier methods*. In subsequent refinements the ring atoms of the phenyl and tolyl groups were constrained to rigid groups of D_{6h} symmetry with aromatic C—C bond distances of 1.397 Å. The tolyl methyl carbon—carbon distances were initially idealized at 1.52 Å but were not constrained to the group. The atomic scattering factors for non-hydrogen atoms were from the tabulation in International Tables for X-ray Crystallography [9]; the values for hydrogen were those of Stewart et al. [10]. The anomalous dispersion terms of Cromer [11] for nickel and phosphorus were applied to the calculated structure factors. Refinement of the structure continued by the method of full-matrix least-squares, minimizing $\Sigma w\Delta^2$ ($w = 4F_o^2/\sigma^2(F_o^2)$, $\Delta = ||F_o| - |F_c||$). The agreement indices $R = (\Sigma\Delta/\Sigma|F_o|)$ and $R_w = ([\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2})$ were 0.166 and 0.224, respectively, after the first cycle of refinement which included the entire molecule of complex. The values were reduced to 0.096 and 0.129, respectively, after another two cycles of refinement in which anisotropic thermal parameters were assigned to the atoms in the inner coordination sphere and individual isotropic thermal parameters to the group atoms.

A difference Fourier synthesis at this point revealed considerable electron density about a position of twofold symmetry in the lattice. The solvent system used for crystallization of the material was cyclohexane/benzene/THF 1/2/2. We were unable to decide which solvent molecule in the ratio Ni-complex/solvent 2/1 was present on the basis of elemental analyses for C and H. Although the low solubility of the complex in suitable solvents made the determination difficult, NMR spectra were interpreted to favor the presence of THF. Indeed a reasonable position for the THF molecule could be obtained from the difference Fourier map. However, neither this model for THF nor more elaborate ones subsequently devised refined properly; excessively high thermal parameters on the atoms of the THF molecule invariably resulted. These high thermal parameters on the solvent molecule may result from partial occupancy as well as from possible disorder. From this point onward we elected to position the THF molecule in a manner that best fit the electron density map but not to vary its position.

Difference Fourier maps of planes where hydrogen atoms were expected revealed reasonable hydrogen- atom positions for all of the tolyl methyl groups, despite the high thermal motion exhibited by these atoms. These hydrogen atom positions were idealized using C—H distances of 1.0 Å and tetrahedral geometry. Hydrogen atom positions for the aromatic rings were idealized using a C—H distance of 1.0 Å and D_{6h} symmetry. The temperature factor of each hydrogen

---

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

atom was set equal to that of the carbon atom to which it is attached. The two ethylenic hydrogen atoms could not be located. A fixed contribution for all hydrogen atoms and the THF molecule was included in all further structure factor calculations. Two final cycles of refinement resulted in final values of 0.093 and 0.129 for R and R_w.

In the final cycle no parameter shifted by more than 0.7 of its estimated standard deviation. The standard deviation of an observation of unit weight is 4.5 e. An analysis of $\Sigma w(|F_o|-|F_c|)^2$ as a function of setting angles, $|F_o|$, and Miller indices revealed that agreement was worst at low scattering angles. This is to be expected in view of our inadequate treatment for the scattering of the rather ill-defined solvent molecule. Although some improvement in R indices might have been achieved through the assignment of anisotropic thermal parameters to the methyl C atoms of the tolyl groups, it was felt that the structural parameters of interest would not have been better defined. In this regard the geometry of the inner coordination sphere proved to be insensitive to the model used for the solvent scattering. The maximum density on a final difference Fourier synthesis was 0.8(2) $e/\text{Å}^3$ about 20% of that of a carbon atom in previous Fourier syntheses.

The positional and thermal parameters obtained from the last cycle of refinement are listed in Table 1 with the associated standard deviations estimated from the inverse matrix. Table 2 lists the positions of the ring atoms derived from the data of Table 1. The two tables which give (a) the idealized positional coordinates for all hydrogen atoms, and (b) a listing of 10 × $|F_o|$ and 10 × $|F_c|$ for all those reflections used in refinement of the structure, are available*.

Description and discussion of the structure

The numbering scheme for the atoms of interest in the structure is presented in Fig. 1. All figures display the 50% probability ellipsoids for thermal motion. The numbering scheme is analogous to that used in the isoelectronic azo struc-

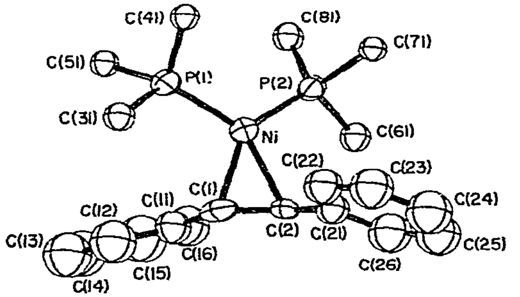

Fig. 1. The structurally significant atoms of the molecule, $Ni(PTol_3)_2(PhHC{=}CPhH)$, showing the labelling scheme. The 50% probability ellipsoids of thermal vibration are shown.

---

* These data have been deposited as Document No. 02331 with the A.S.I.S. National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N.Y. 10022. A copy may be secured by citing the document number and remitting $2.00 for a microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to CCMIC-NAPS.

TABLE 1

POSITIONAL, GROUP, AND THERMAL PARAMETERS FOR $Ni(PTol_3)_2(PhHC{=}CPhH)\cdot 0.5(C_4H_8O)$

Atom	x [a]	y	z	β_{11} [b,c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.03099(1)	−0.10287(7)	0.20330(10)	18.1(8)	13.5(5)	24.0(9)	0.7(4)	1.1(6)	−3.2(5)
P(1)	0.1043(2)	−0.0913(1)	0.2848(2)	21.8(13)	11.4(7)	21.5(13)	1.5(8)	2.6(10)	−1.6(7)
P(2)	0.0694(2)	−0.1219(1)	0.1023(2)	22.2(13)	11.9(7)	22.3(13)	1.8(8)	0.8(11)	0.3(7)
C(1)	−0.0567(6)	−0.0834(5)	0.2521(8)	10(5)	16(3)	43(6)	−2(3)	4(5)	−11(4)
C(2)	−0.0700(7)	−0.1122(6)	0.1893(8)	16(5)	21(3)	44(6)	2(3)	8(5)	−4(4)

Group	x_c [d]	y_c	z_c	δ	ϵ	η
Ring 1	−0.0749(3)	0.0251(3)	0.2578(4)	2.022(31)	−1.799(6)	0.325(31)
Ring 2	−0.0875(4)	−0.2213(3)	0.1967(5)	−1.628(22)	−1.980(7)	0.049(21)
Ring 3	0.0295(3)	−0.1099(2)	0.4297(3)	−0.042(6)	−2.909(6)	2.080(6)
Ring 4	0.2398(3)	−0.1620(2)	0.3020(3)	−0.132(22)	−1.802(5)	0.438(23)
Ring 5	0.1739(3)	0.0203(2)	0.2927(2)	−1.981(5)	−3.148(5)	3.094(5)
Ring 6	−0.0433(3)	−0.1140(3)	−0.0172(3)	−3.067(6)	2.949(6)	0.804(6)
Ring 7	0.1211(3)	−0.2380(2)	0.0806(3)	−1.102(9)	2.216(6)	−0.233(9)
Ring 8	0.1901(3)	−0.0493(2)	0.0427(3)	2.135(16)	1.918(5)	−1.470(16)

[a] Numbers in parentheses here and throughout the paper are estimated standard deviations in the least significant digits. [b] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. The values of β have been multiplied by 10^4. [c] The minimum, intermediate, and maximum root-mean-square amplitudes of vibration (Å) for the anisotropic atoms are: Ni, 0.183(4), 0.201(4), 0.235(4); P(1), 0.180(7), 0.211(6), 0.218(6); P(2), 0.192(7), 0.210(6), 0.217(6); C(1), 0.14(3), 0.19(3), 0.32(2); and C(2), 0.16(3), 0.26(2), 0.31(2). [d] These quantities have been defined previously (see ref. 15).

TABLE 2

POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR PHENYL AND TOLYL RING CARBON ATOMS AND THE FIXED PARAMETERS FOR THE TETRAHYDROFURAN MOLECULE

Atom	x	y	z	B(Å^2)
C(11)	−0.0654(5)	−0.0277(3)	0.2527(6)	4.1(3)
C(12)	−0.0828(5)	−0.0059(4)	0.3150(4)	5.4(4)
C(13)	−0.0923(6)	0.0469(4)	0.3201(5)	7.5(4)
C(14)	−0.0845(6)	0.0779(3)	0.2629(7)	8.1(5)
C(15)	−0.0671(5)	0.0561(4)	0.2006(5)	7.1(5)
C(16)	−0.0576(5)	0.0033(4)	0.1955(4)	5.5(4)
C(21)	−0.0802(6)	−0.1681(3)	0.1953(7)	4.8(4)
C(22)	−0.0592(6)	−0.1957(5)	0.2523(5)	7.4(5)
C(23)	−0.0665(7)	−0.2489(5)	0.2536(6)	9.7(6)
C(24)	−0.0947(7)	−0.2744(3)	0.1980(8)	9.3(6)
C(25)	−0.1157(6)	−0.2468(5)	0.1411(6)	8.9(5)
C(26)	−0.1085(6)	−0.1936(5)	0.1397(5)	8.1(6)
C(31)	0.0649(4)	−0.1002(4)	0.3695(4)	3.5(3)
C(32)	0.0447(5)	−0.1500(3)	0.3855(5)	4.5(4)
C(33)	0.0093(5)	−0.1597(3)	0.4456(5)	5.3(4)
C(34)	−0.0059(5)	−0.1195(4)	0.4899(4)	5.8(4)
C(35)	0.0143(5)	−0.0697(3)	0.4739(4)	5.5(4)
C(36)	0.0497(5)	−0.0600(3)	0.4137(5)	4.4(4)
C(37)	−0.0442(9)	−0.1304(7)	0.5550(9)	8.4(5)
C(41)	0.1796(4)	−0.1337(3)	0.2951(5)	3.5(3)
C(42)	0.2079(4)	−0.1584(3)	0.2389(3)	3.7(3)
C(43)	0.2681(4)	−0.1866(3)	0.2457(4)	3.6(3)
C(44)	0.3001(4)	−0.1902(3)	0.3089(5)	3.9(3)
C(45)	0.2718(5)	−0.1656(4)	0.3652(3)	4.3(4)
C(46)	0.2116(5)	−0.1374(3)	0.3583(4)	4.7(4)
C(47)	0.3652(7)	−0.2211(5)	0.3164(8)	5.3(4)
C(51)	0.1454(4)	−0.0286(3)	0.2894(4)	2.9(3)
C(52)	0.1029(3)	0.0143(4)	0.2915(4)	3.7(3)
C(53)	0.1314(4)	0.0633(3)	0.2948(5)	4.3(3)
C(54)	0.2024(5)	0.0693(3)	0.2961(4)	5.0(4)
C(55)	0.2449(3)	0.0263(4)	0.2940(4)	4.4(3)
C(56)	0.2164(5)	−0.0226(3)	0.2906(4)	4.1(3)
C(57)	0.2362(9)	0.1227(6)	0.3015(8)	7.5(4)
C(61)	0.0069(4)	−0.1186(4)	0.0329(4)	3.6(3)
C(62)	−0.0228(5)	−0.0710(3)	0.0195(5)	4.5(4)
C(63)	−0.0729(5)	−0.0664(3)	−0.0306(5)	6.0(4)
C(64)	−0.0935(4)	−0.1094(4)	−0.0673(5)	6.6(4)
C(65)	−0.0638(5)	−0.1570(3)	−0.0540(5)	6.9(4)
C(66)	−0.0137(5)	−0.1616(3)	−0.0039(5)	5.7(4)
C(67)	−0.1506(10)	−0.1049(7)	−0.1215(9)	8.7(5)
C(71)	0.1014(5)	−0.1871(2)	0.0904(5)	3.0(3)
C(72)	0.0780(4)	−0.2251(4)	0.1345(4)	4.0(3)
C(73)	0.0977(5)	−0.2759(3)	0.1247(4)	4.3(3)
C(74)	0.1407(5)	−0.2888(3)	0.0707(5)	4.1(3)
C(75)	0.1641(4)	−0.2508(4)	0.0266(4)	6.1(4)
C(76)	0.1444(5)	−0.2000(3)	0.0364(4)	5.8(4)
C(77)	0.1635(7)	−0.3445(5)	0.0609(7)	5.0(4)
C(81)	0.1375(4)	−0.0805(3)	0.0667(5)	3.1(3)
C(82)	0.1816(5)	−0.0565(3)	0.1124(3)	3.9(3)
C(83)	0.2343(5)	−0.0252(3)	0.0884(4)	4.4(4)
C(84)	0.2428(4)	−0.0180(3)	0.0187(5)	4.7(4)
C(85)	0.1986(5)	−0.0421(4)	−0.0270(3)	5.0(4)
C(86)	0.1450(4)	−0.0733(3)	−0.0030(4)	4.1(3)
C(87)	0.2986(9)	0.0165(6)	−0.0077(9)	7.9(5)
C(T1)	0.210	−0.212	0.380	15
C(T2)	−0.228	−0.225	0.458	15
O(T)	−1/4	−1/4	0.34	15

ture [4]. For the sake of clarity, only the six α carbon atoms of the phosphines are presented. The numbering for all rings starts at the α carbon atom and works around the ring, numbering the tolyl methyl carbon atoms last. Hydrogen

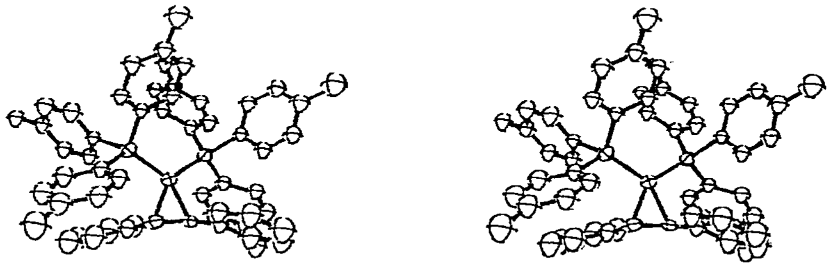

Fig. 2. Stereo view of the molecule, $Ni(PTol_3)_2(PhHC{=}CPhH)$ showing intramolecular packing. Hydrogen atoms are omitted for the sake of clarity.

atoms have the same number as the carbon atoms to which they are attached, with 1, 2, or 3 indicating the three methyl hydrogen atoms on each tolyl ring. Figure 2 is a stereo view of the entire molecule and displays the intramolecular packing of the aromatic rings. Note that adjacent rings are roughly perpendicular and interlocking in this structure while they were parallel in the azo structure. Figure 3 presents the packing diagram for the unit cell. One can discern the intermolecular packing and the positions of the THF molecules of solvation at 1/4, 1/4, z and 3/4, 3/4, z. Intermolecular contacts are normal, the shortest between non hydrogen atoms being 3.36(2) Å between two C(75) atoms related by a twofold axis. Relevant interatomic distances and angles are presented in Tables 3 and 4. Table 5 presents data on various dihedral angles.

As in the azo structure, the molecule possesses essentially C_2 symmetry. If one regards the olefin as monodentate, then the nickel atom is three coordinate.

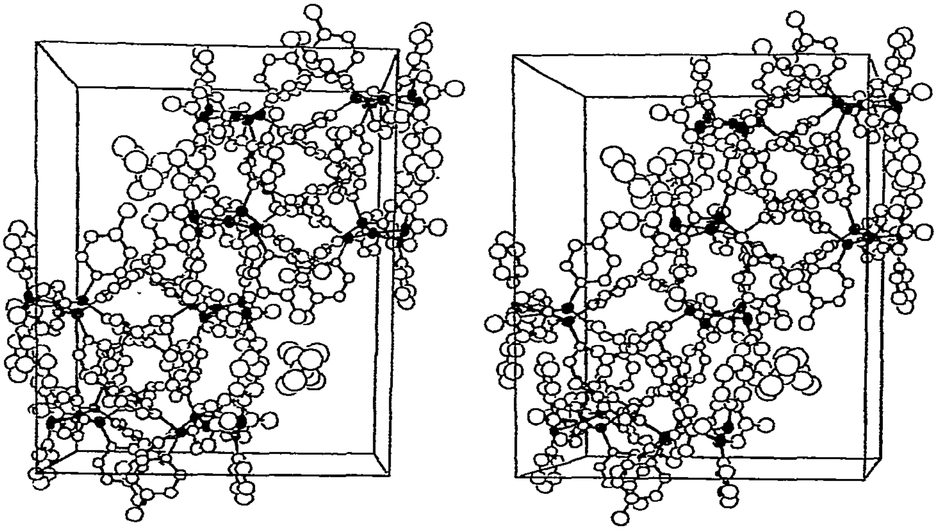

Fig. 3. Stereo view of the unit cell of $Ni(PTol_3)_2(PhHC{=}CPhH)\cdot 0.5(C_4H_8O)$ showing intermolecular packing. Inner coordination spheres are darkened and hydrogen atoms are omitted for the sake of clarity. The x direction is to the right, the y direction is vertical, and z is out of the page.

TABLE 3

SELECTED DISTANCES (Å) IN $Ni(PTol_3)_2(PhHC{=}CPhH)\cdot 0.5(C_4H_8O)$ [a]

Bonded distances			Non-bonded distances		
Ni—P(1)	2.175(4)	2.181(4) [b]	P(1)—C(1)	3.219(13)	3.224(14)
Ni—P(2)	2.186(4)		P(2)—C(2)	3.230(14)	
Ni—C(1)	2.030(13)	2.019(13)	P(1)—P(2)	3.750(5)	
Ni—C(2)	2.008(13)		C(1)—C(16)	2.527(18)	2.524(20)
C(1)—C(2)	1.471(19)		C(2)—C(22)	2.521(20)	
C(1)—C(11)	1.467(16)	1.474(17)	C(1)—C(12)	2.432(28)	2.247(24)
C(2)—C(21)	1.480(17)		C(2)—C(26)	2.461(20)	
P(1)—C(31)	1.854(8)	1.843(11)	C(1)—C(22)	2.936(19)	2.984(19)
P(1)—C(41)	1.828(8)		C(2)—C(16)	3.031(19)	
P(1)—C(51)	1.854(8)				
P(2)—C(61)	1.837(9)				
P(2)—C(71)	1.831(8)		C(1)—C(21)	2.523(17)	2.531(17)
P(2)—C(81)	1.854(9)		C(2)—C(11)	2.539(17)	
C(34)—C(37)	1.514(20)	1.529(20)			
C(44)—C(47)	1.514(16)				
C(54)—C(57)	1.549(18)				
C(64)—C(67)	1.550(21)				
C(74)—C(77)	1.535(15)				
C(84)—C(87)	1.509(19)				

[a] The fixed parameters used to describe the molecule of THF resulted in O—C(1), C(1)—C(2) and C(2)—C(2)′ distances of 1.49, 1.61, and 1.56 Å, respectively. [b] These are average quantities. The estimated standard deviation is the larger of an individual standard deviation or the standard deviation of a single observation as calculated from the mean.

The five atoms of the inner coordination sphere are decidedly less planar than in the azo structure, with a dihedral angle of −18.5(9)° between the P(1)—Ni—P(2) and C(2)—Ni—C(1) planes. This decreased planarity is reflected in the deviations of these atoms from the weighted least-squares plane 1 (Table 6). This

TABLE 4

SELECTED INTRAMOLECULAR BOND ANGLES (DEG.) IN $Ni(PTol_3)_2(PhHC{=}CPhH)\cdot 0.5(C_4H_8O)$ [a]

P(1)—Ni—P(2)	118.6(2)
C(1)—Ni—C(2)	42.7(6)
P(1)—Ni—C(1)	99.9(4)
P(2)—Ni—C(2)	100.6(5)
Ni—C(1)—C(2)	67.9(8)
Ni—C(2)—C(1)	69.4(7)
Ni—C(1)—C(11)	110.5(9)
Ni—C(2)—C(21)	104.0(9)
C(1)—C(11)—C(12)	116.2(11)
C(2)—C(21)—C(26)	117.6(12)
C(1)—C(11)—C(16)	123.8(11)
C(2)—C(21)—C(22)	122.3(11)
C(1)—C(2)—C(21)	117.5(13)
C(2)—C(1)—C(11)	119.6(12)
Ni—P(1)—C(31)	112.0(3)
Ni—P(1)—C(41)	121.4(3)
Ni—P(1)—C(51)	116.8(3)
Ni—P(2)—C(61)	116.1(3)
Ni—P(2)—C(71)	116.5(3)
Ni—P(2)—C(81)	117.2(3)

[a] The fixed parameters used to describe the molecule of THF resulted in C(1)—O—C(1)′, O—C(1)—C(2) and C(1)—C(2)—C(2)′ bond angles of 116, 104 and 107°, respectively.

TABLE 5

SELECTED INTRAPLANAR AND VECTOR-PLANE-NORMAL ANGLES (DEG.) IN $Ni(PTol_3)_2 \cdot (PhHC{=}CPhH) \cdot 0.5(C_4H_8O)$

Dihedral angles [a]		Vector-plane-normal angles	
P(1)—Ni—P(2) C(2)—Ni—C(1)	— 18.5(9)	C(1)—C(2) Ni—P(1)—P(2)	108.4(9)
P(2)—Ni—C(2) C(1)—Ni—P(1)	11.6(5)	C(1)—C(2) C(11)—C(13)—C(15)	114.3(8)
C(11)—C(1)—C(2) C(21)—C(2)—C(1)	17.3(11)	C(2)—C(1) C(21)—C(23)—C(25)	103.0(8)
C(11)—C(13)—C(15) C(11)—C(1)—C(2)	— 28.1(11)	C(1)—C(11) C(11)—C(13)—C(15)	89.9(8)
Ni—C(1)—C(2) C(1)—C(2)—C(11)	—101.8(11)	C(2)—C(21) C(21)—C(23)—C(25)	86.8(10)
C(21)—C(25)—C(23) C(21)—C(2)—C(1)	— 16.7(12)	C(11)—C(1) Ni—C(1)—C(2)	31.6(13)
Ni—C(1)—C(2) C(1)—C(2)—C(21)	95.5(11)	C(21)—C(2) Ni—C(1)—C(2)	28.0(13)
C(11)—C(13)—C(15) C(21)—C(25)—C(23)	— 38.0(60		

[a] For definitions of angles, see ref. 4.

decreased planarity is also clearly evident in Fig. 4, which is a view of the atoms of interest looking down the N=N bond in the azo structure and the C=C bond in the stilbene structure.

Figure 4 also demonstrates two other effects. First, the azobenzene in the

TABLE 6

DEVIATIONS (Å) FROM WEIGHTED LEAST-SQUARES PLANES [a]

Atom	Plane 1	Plane 2	Plane 3
Ni	0.002(2)		
P(1)	—0.006(3)		
P(2)	0.003(3)		
C(1)	0.202(14)	0.184(12)	—0.140(13)
C(2)	—0.259(15)	—0.326(13)	0.143(14)
C(11)		0.097(10)	
C(12)		0.099(11)	
C(13)		0.009(12)	
C(14)		—0.083(11)	
C(15)		—0.085(11)	
C(16)		0.005(10)	
C(21)			0.030(12)
C(22)			—0.015(12)
C(23)			—0.047(12)
C(24)			—0.033(14)
C(25)			0.012(13)
C(26)			0.044(11)

[a] Plane Equation: $Ax + By + Cz - D = 0$ with x, y and z in orthorhombic coordinates; A, B, C, and D in angstroms.

Plane	A	B	C	D
1	0.860	25.434	—4.485	—3.504
2	19.229	1.431	3.381	—0.541
3	18.050	—2.060	—7.410	—2.579

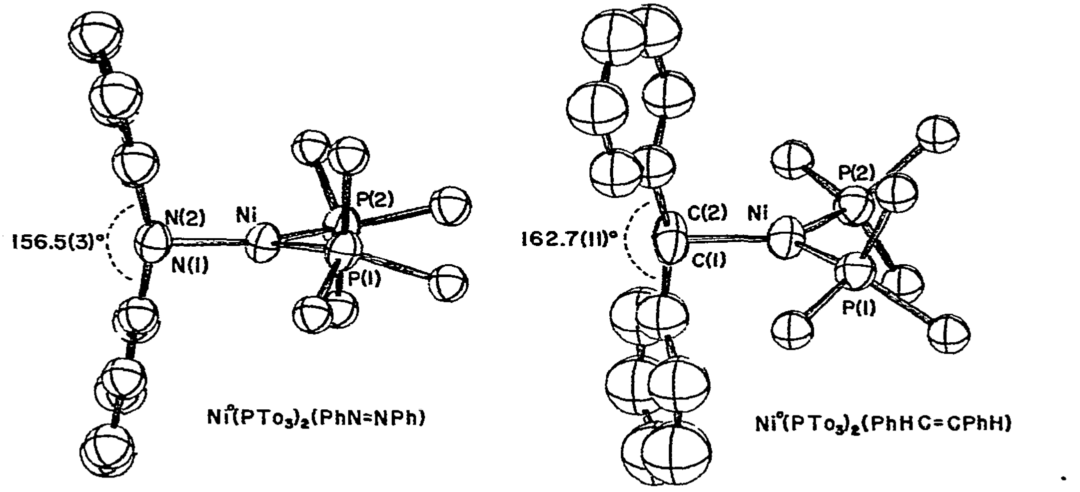

Fig. 4. Illustration of the nickel phosphine complexes of *trans*-stilbene and azobenzene as viewed down the unsaturated C=C and N=N bonds.

azo complex can be described by two planes; there is very little twist about the N—C bonds so the phenyl groups are almost coplanar with the N(1)—N(2) bond. In the stilbene complex there is a considerable twist about the olefin—phenyl group C—C bond as indicated by the intraplanar angles of −28.1(11)° for C(11)C(1)C(2)—C(11)C(13)C(15) and −16.7(12)° for C(21)C(2)C(1)—C(21)-C(25)C(23). These angles in the azo structure are 3.0(4)° and 1.0(3)°, respectively. This twisting of the phenyl groups may be attributed to the minimization of contact interactions between the ortho hydrogen atoms on the ring and the *cis* olefinic hydrogen atoms. One can estimate positions for the olefinic hydrogen atoms by requiring that they lie in the plane formed by the double bond and the *cis*-α-phenyl carbon atom with a C=C—H angle equal to the geminal C=C—C angle. This estimate results in H(1)—H(22) and H(2)—H(16) contact distances of 2.02 and 2.28 Å, respectively. If the phenyl groups had not twisted, these distances would be approximately 1.85 Å.

The second effect which is of greater importance to the description of bonding is that the phenyl groups are not bent back away from the nickel atom as much as they are in the azo structure. The intraplanar angle defined by C(11)C(1)C(2)—C(21)C(2)C(1) is 17.3(11)°, but in the azo structure the analogous angle is 23.5(3)°. This indicates that less electron density is being transferred into antibonding orbitals on the olefin molecule than into azobenzene.

The Ni—P distances for P(1) and P(2) are 2.175(4) and 2.186(4) Å, respectively, somewhat shorter than in the azo complex [Ni—P = 2.195(3) and 2.201(3) Å]. This result is rather unexpected. It has been demonstrated [12] in the *trans*-dichloro- and *trans*-dibromo bis (triethylphosphine)platinum system that the bromo complex, which has a greater electron density on the metal, has longer metal—phosphorus bonds. Decreased π-backbonding in the case of the stilbene complex results in a greater electron density on the metal. There should be less σ donation from the phosphines and consequently a longer, weaker metal—phosphine bond. One might argue that because the olefin is π-bonded, there is a symbiotic effect which enhances the formation of π bonds to the phosphines and this π bonding is reflected in the shorter metal—phosphorus distances. While this might be the case, the unexpected result can also be rationalized on the basis of steric arguments. It has already been pointed out that the packing of the aromatic rings is markedly different in the stilbene complex. This difference causes the P(1)—Ni—P(2) angle to open from 107.4(1)° in the azo complex to 118.6(2)° for the stilbene complex. This increased angle may allow the phosphines to approach the nickel atom more closely. The P—C(n1) and C(n4)—C(n7) distances and the Ni—P—C(n1) angle where $n = 3$ to 8 are comparable with the values obtained for the azo complex.

The Ni—C(1) and Ni—C(2) distances are 2.030(13) and 2.008(13) Å respectively, giving an average value of 2.019(14) Å. The C(1)—C(2) distance is 1.471(19) Å. These bond distances are equivalent to those of the triphenylphosphine ethylene complex [5]. Using the azo structure as a model and a covalent radius of C of 0.07 Å greater than that of N [13] one would predict, assuming all other factors being equal, that these distances would be 2.00 and 1.51 Å, respectively.

These crystallographic results are consistent with spectroscopic measurements and chemical observations. It has been shown previously [4] that isocyanide stretching frequencies for complexes of the type $Ni(t\text{-}BuN{\equiv}C)_2(Un)$ are an indication of the degree of backbonding to the unsaturated molecule, Un; higher stretching frequencies indicate lower electron density on the metal. The frequencies $\nu(N{\equiv}C) = 2168$, 2100, and 2080 cm^{-1} for Un = azobenzene, *trans*-stilbene, and *cis*-stilbene, respectively, indicate that these molecules accept progressively less electron density from the nickel; azobenzene forms a better π bond than *trans*-stilbene, which is better than *cis*-stilbene.

This trend is also observed in exchange reactions converting one complex into another. Azobenzene easily displaces *trans*-stilbene and both of these molecules displace *cis*-stilbene from the respective isocyanide complexes. While both azobenzene and *trans*-stilbene easily displace cyclooctadiene from the starting material, $Ni(COD)_2$, *cis*-stilbene displaces it only with great difficulty. Addition of up to a hundred-fold excess of *trans*-stilbene to a tetrahydrofuran solution of bis(tri-*p*-tolylphosphine)(azobenzene)nickel(0) causes little change in the visible spectrum.

These structural, spectroscopic, and chemical results may be rationalized in several ways. A simple approach is based on the activation of the double bond. Classically, the method used for the formation of stronger π complexes has been the "activation" of the double bond by the addition of highly electronegative, electron-withdrawing groups to the olefin. In the azo compound, compared with the olefin, the double bond has been activated not by substituents, but by making the atoms forming the double bond more electronegative. This *intrinsic* activation has the same effect as *extrinsic* activation by substituents in that it causes a stronger π backbond.

Jaffe and coworkers [14] have calculated the one electron orbital energy level diagrams for stilbene, benzalaniline, and azobenzene shown in Fig. 5. These LCAO calculations indicate that the highest occupied molecular orbital (HOMO), from which there would be σ forward donation to the metal, is of

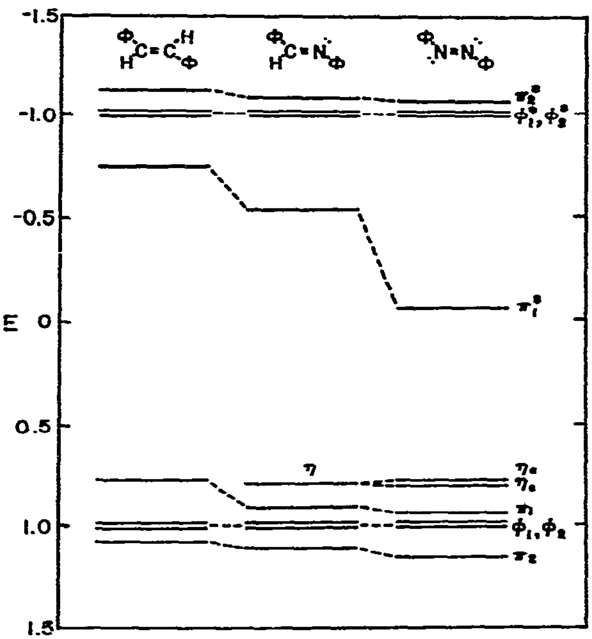

Fig. 5. One-electron orbital energy level diagrams for stilbene, benzalaniline and azobenzene (from ref. 11). The LCAO orbital energy is expressed in β, the resonance integral for the benzene rings. In stilbene, π_1 is localized on the double bond as are the η orbitals in benzalaniline and azobenzene. The π_1^* orbital is localized on the double bond for all three species.

approximately equal energy for the three species. This level is localized mostly on the double bond for all three species. The lowest unoccupied molecular orbital (LUMO) in each case is the π antibonding orbital localized on the double bond. It is of much lower energy in azobenzene than in stilbene. This lowering should greatly facilitate the π-backbonding to the unsaturated molecule, a prediction which is in accord with observation.

The electronic absorption observed in the visible region for the azobenzene complex can be assigned to the $n \rightarrow \pi^*$ transition. In free azobenzene, the $n \rightarrow \pi^*$ absorption is forbidden by symmetry and is therefore weak. After complexation this symmetry restriction is relaxed by the bending back of the phenyl groups and the absorption is more intense. The absorption is red shifted by the π backbonding which stabilizes the antibonding orbital, but it retains its breadth which is characteristic of azo $n \rightarrow \pi^*$ transitions.

The simple one electron calculation predicts no difference between the energy levels of *cis*- and *trans*-stilbene. Experimentally it is found that the lowest observed transition in the electronic spectrum is 294 nm for *trans*-stilbene and 272 nm for *cis*-stilbene, in accord with more sophisticated calculations [14b]. This transition, assigned to $\pi_1 \rightarrow \pi_1^*$ in both cases, indicates that the LUMO is higher in energy in *cis*-stilbene than in *trans*-stilbene, resulting in a poorer π-backbond. This again is in accord with the chemical and spectroscopic results reported here.

Acknowledgment

We wish to thank the U.S. National Institutes of Health for their support of this work.

References

1 R.S. Dickson and J.A. Ibers, J. Organometal. Chem., 36 (1972) 191.
2 R.S. Dickson and J.A. Ibers, J. Amer. Chem. Soc., 94 (1972) 2988; R.S. Dickson, J.A. Ibers, S. Otsuka, and Y. Tatsuno, J. Amer. Chem. Soc., 93 (1971) 4636.
3 J.K. Stalick and J.A. Ibers, J. Amer. Chem. Soc., 92 (1970) 5333.
4 S.D. Ittel and J.A. Ibers, J. Organometal. Chem., 57 (1973) 389.
5 C.D. Cook, C.H. Kóo, S.C. Nyburg, and M.T. Shiomi, Chem. Commun., (1967) 426; W. Dreissig and H. Dietrich, Acta Crystallogr., Sect. B, 24 (1968) 108.
6 G. Wilke, Angew. Chem., 72 (1960) 581.
7 J. Casanova, N.D. Werner, and R.E. Schuster, J. Org. Chem., 31 (1966) 3473.
8 R.J. Doedens and J.A. Ibers, Inorg. Chem., 6 (1967) 204.
9 International Tables for X-Ray Crystallography, Vol. 4, Kynoch Press, Birmingham, in press.
10 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
11 D.T. Cromer, Acta Crystallogr., 18 (1965) 17.
12 G.G. Messmer and E.L. Amma, Inorg. Chem., 5 (1966) 1775.
13 L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, N.Y., 1960.
14 (a) H.H. Jaffe, S.J. Yeh and R.W. Gardner, J. Mol. Spectrosc., 2 (1958) 120;
(b) D.L. Beveridge and H.H. Jaffe, J. Amer. Chem. Soc., 87 (1965) 5340.
15 S.J. La Placa and J.A. Ibers, Acta Crystallogr., 18 (1965) 511.