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THE PREPARATION AND STRUCTURE OF BIS(TRI-*p*-TOLYLPHOSPHINE)(AZOBENZENE)NICKEL(0), $Ni[P(C_6H_4CH_3)_3]_2[C_6H_5N{=}NC_6H_5]$

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SUMMARY

The compound, bis(tri-*p*-tolylphosphine)(azobenzene)nickel(0), $Ni[P(C_6H_4CH_3)_3]_2[C_6H_5N{=}NC_6H_5]$, has been prepared by the reaction of tri-*p*-tolylphosphine and azobenzene with bis(1,5-cyclooctadiene)nickel(0) in hexane. The structure of the complex has been determined at room temperature from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final R factor on F of 6.6% based on 3516 observations above background. The material crystallizes in the triclinic space group C_i^1-$P\bar{1}$, with two molecules in a cell of dimensions $a = 12.448(11)$, $b = 17.671(20)$, $c = 12.226(13)$ Å, α 95.79(5), β 118.34(3), γ 97.17(4)°. The Ni atom has trigonal coordination if the azobenzene is regarded as a monodentate ligand. The inner coordination sphere is essentially planar, with the two nitrogen atoms equidistant from the metal atom. The structure is compared with that of $Ni[(CH_3)_3C{-}N{\equiv}C]_2[C_6H_5N{=}NC_6H_5]$, a similar complex studied earlier in this laboratory. Observed differences in the coordinated azobenzenes have been related to observed spectral differences.

INTRODUCTION

The bonding of olefins and acetylenes to transition metals has been adequately described by the Dewar, Chatt, Duncanson[1] model, or modifications thereof[2]. This model, which involves donation of electron density from the π-bonding orbitals and acceptance of electron density into the π^*-orbitals, predicts lengthening of the unsaturated bond and bending of the substituent groups away from the metal. This lowering of bond order causes acetylenes to become non-linear, and olefins to become nonplanar. Precise structural studies have confirmed these predicted effects.

The π-bonding scheme of olefins and acetylenes may be carried over into non-carbon–carbon unsaturated bonds. This type of bonding has been postulated for organic carbonyls[3] ($R_2C{=}O$), substituted methylenimines[3] ($R_2C{=}NR$), carbon dioxide[4], carbon disulfide[5], disulfur[6], dioxygen[7], nitroso compounds[8] and substituted diazenes[9–12] (RN=NR). Structural studies have been completed on the latter five types of complexes, with all observed effects conforming to the predictions of electron density being transferred into π^*-orbitals on the ligand.

In early 1971, Otsuka and coworkers[9], and Klein and Nixon[10] simultaneously reported the formation of nickel(0) π-complexes of the diphenyl-substituted diazene, azobenzene. A short time later, Klein also reported a cobalt(0) π-complex[11]. The π-bonded structure, which had been postulated for diazene complexes but never found experimentally[12], was predicted on the basis of chemical displacement reactions and spectroscopic evidence. The compound, $Ni[(CH_3)_3C{-}N{\equiv}C]_2(PhN{=}NPh)$, where $Ph{=}C_6H_5$, has been the subject of a crystallographic study[12] which confirmed the π-bonded type of structure. Since this represents the first π-bonded diazene complex confirmed by diffraction analysis it is of interest to search for other such systems and through diffraction and spectroscopic means attempt to determine factors which account for this mode of bonding. The structure of $Ni(PTo_3)_2(PhN{=}NPh)$, where To = *p*-tolyl, is reported in this paper. This analogue of Klein and Nixon's compound, $Ni(PPh_3)_2(PhN{=}NPh)$, was chosen for crystallographic reasons. For the purpose of additional comparisons, the determination of the structure of $Ni(PTo_3)_2$(*trans*-PhHC=CPhH) is currently in progress.

EXPERIMENTAL

The compound, $Ni(PPh_3)_2(PhN{=}NPh)$, was prepared by the method of Klein and Nixon[10]. The same material was prepared by the method of Otsuka *et al.*,[9] substituting triphenylphosphine for the t-butylisocyanide. The material was crystallized from THF as air sensitive, deep carmine rhombs. Crystals from toluene–hexane were deep carmine plates.

$Ni(PTo_3)_2(PhN{=}NPh)$ was prepared by the method of Otsuka *et al.*[9], substituting tri-*p*-tolylphosphine for the isocyanide. It was crystallized from diethyl ether as air-sensitive, dark red plates. (Analysis: Found C, 0.7639; H, 0.0628; N, 0.026. Calcd.: C, 0.7633; H, 0.0617; N, 0.033 %.)

Crystals for data collection were handled in a nitrogen filled glove bag and mounted in dried, nitrogen filled glass or quartz capillaries. All compounds for the spectral study were prepared by the method of Otsuka *et al.*[9] They were dissolved in toluene, and the visible spectra were recorded on a Cary 14 spectrophotometer.

Crystal data

(a) *$Ni(PPh_3)_2(PhN{=}NPh)$ from toluene–hexane.* Monoclinic; $a = 14.73$, $b = 13.87$, $c = 19.02$ Å, $\beta = 94.2°$; $V = 3876$ Å^3; $d_{calc} = 1.31$ g·cm^{-3} for $Z = 4$. Precession and Weissenberg photographs taken with Cu-K_α radiation showed systematic absences of hkl when $h+k \neq 2n$, $h0l$ when $l \neq 2n$ ($h \neq 2n$), and $0k0$ when $k = 2n$, indicative of the monoclinic space groups $C2/c$ or Cc.

Examination of a number of crystals by the ω-scan technique revealed none which was suitable for analysis. These problems are similar to those reported by another laboratory[13] studying the related complex $Ni[P(CH_3)_3]_2[PhN{=}NPh]$: $NiP_2C_{12}H_{28}N_2$; mol. wt. 393.07; orthorhombic $Pnma$ or $Pn2_1a$; $a = 16.23$; $b = 14.50$, $c = 8.76$ Å; $V = 2061$ Å^3; $d_{calc} = 1.26$ for $Z = 4$.

(b) *$Ni(PTo_3)_2(PhN{=}NPh)$*, $NiP_2C_{54}H_{52}N_2$; mol. wt. = 849.6; triclinic $a = 12.448(11)$, $b = 17.671(20)$, $c = 12.226(13)$ Å, α 95.79(5), β 118.34(3), γ 97.17(4)°; $V = 2310$ Å^3; $d_{calc} = 1.22$ g/cm^3 for $Z = 2$; linear absorption coefficient for Cu-K_α radiation 15.2 cm^{-1}.

The half widths and multiple peaks of narrow-source open-counter ω-scans indicated that most crystals mounted were of unacceptable mosaicity. After a suitable crystal was found, the setting angles of 12 reflections were determined using a narrow vertical slit at a take-off angle of 1°. Cell parameters were then derived by a least-squares procedure.

Data collection was begun on three crystals, and was terminated after 1228, 1892, and 4196 reflections when the standard reflections had fallen off by 20%. Happily, a fourth crystal, bounded by faces of the $\{010\{$, $\{10\bar{1}\}$, and $\{1\bar{1}0\}$ forms with respective distances between faces of 0.31, 0.12, and 0.51 mm (determined by means of a micrometer eyepiece) did not decompose in the X-ray beam. A data set was collected out to $2\theta = 97.5°$ (Cu-K_α), giving 4560 independent reflections. Data collection was terminated because the last shell yielded relatively few intensities above background.

Intensity data were collected with Cu-K_α radiation prefiltered by 0.5 mil Ni foil on a Picker Four Circle Diffractometer. The take-off angle was 3.0°. The counter was positioned 30 cm from the crystal and was preceded by an aperture of dimensions 7 x 7 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 1.2° before the $K_{\alpha 1}$ peak and ending 1.0° after the $K_{\alpha 2}$ peak. Reflections out to $2\theta = 70°$ were scanned at 2° per minute and the remainder at 1° per minute. Background counts of 20 s were taken at each end of the scan range for reflections out to 50° and for 40 s for the remainder.

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 53 observations made for each standard, were one to three times the deviations based on counting statistics alone, but there was no trend in the variations.

All data were processed as described previously[14]. A value of 0.04 was used for p in the estimation of $\sigma(F_o^2)$. Of the observed reflections in the final set of data, 3516 obeyed the condition $F_o^2 > 3\sigma(F_o^2)$ and only these reflections were used in subsequent calculations.

Structure solution and refinement

The structure was solved using conventional Patterson, least-squares, and Fourier methods*. From a Patterson synthesis on the data set obtained from the third crystal, it was possible to locate the nickel and two phosphorus positions in the asymmetric unit. Two cycles of refinement, each followed by a difference Fourier synthesis, led to positions for all non-hydrogen atoms. The agreement factors R ($\Sigma\Delta/\Sigma|F_0|$, $\Delta = ||F_0| - |F_c||$) and R_w ($[\Sigma w \cdot \Delta^2/\Sigma w \cdot F_o^2]^{\frac{1}{2}}$, $w = 4F_o^2/\sigma^2[F_o^2]$) were 0.460 and 0.521, respectively.

Refinement of the structure continued by the method of full-matrix least-squares, minimizing $\Sigma w \cdot \Delta^2$. The phenyl and tolyl rings were constrained to rigid

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* In addition to various local programs for the CDC 6400, computer programs used in this work include local versions of Dewar's FAME program, Zalkin's FORDAP Fourier program, Cahen's AGNOST absorption 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.

groups with aromatic C–C bond distances of 1.397 and methyl C–C bond distances of 1.485 Å. The atomic scattering factors for nickel, phosphorus, nitrogen and carbon used in all calculations were from the tabulation in International Tables for X-ray Crystallography[15]; the values for hydrogen were those of Stewart *et al.*[16]. The anomalous dispersion terms of Cromer[17] for nickel, phosphorus and nitrogen were applied to the calculated structure factors.

Two cycles of refinement, in which all non-group atoms were assigned isotropic thermal parameters and each of the groups an overall thermal parameter, resulted in values of 0.234 and 0.299 for R and R_w, respectively. After correction for absorption, with calculated transmission factors ranging from 0.602 to 0.839, another cycle of isotropic refinement followed by a cycle in which all non-group atoms were allowed to vibrate anisotropically reduced R and R_w to 0.138 and 0.180. A difference Fourier map revealed peaks which could be ascribed to the aromatic and methyl hydrogen atoms of the phenyl and tolyl rings. At this point refinement was discontinued because it was felt that the hydrogen contributions would not lower the R factors to acceptable values. The poor quality of the data set, resulting from crystal decomposition, was deemed to be the probable cause of difficulty, so a new data collection was undertaken at this time.

The data set from the fourth crystal was corrected for absorption to give transmission factors ranging from 0.582 to 0.841. Refinement was begun starting with the parameters from the previous data set. Two cycles of isotropic refinement followed by one cycle with the five non-group atoms vibrating anisotropically and another in which the six tolyl (methyl) carbons were also allowed to vibrate anisotropically resulted in R and R_w of 0.095 and 0.118 respectively. A difference Fourier map revealed all hydrogen atom positions, including those around the tolyl carbon atoms despite the very high thermal motions exhibited by these atoms. These hydrogen atom positions were idealized using C–H distances of 1.0 Å, D_{6h} symmetry for the rings and tetrahedral geometry for the tolyl (methyl) hydrogens. The temperature factor of each hydrogen atom was set equal to that of the carbon atom to which it was attached. Fixed contributions for all hydrogen atoms were included in all further structure factor calculations. In two final cycles, the refinement converged to R 0.066 and R_w 0.091.

In the final cycle, no parameter shifted by more than 0.3 of its estimated standard deviation. The standard deviation of an observation of unit weight is 3.40 *e*. An analysis of $\Sigma w(|F_o|-|F_c|)^2$ as a function of setting angles, magnitude of $|F_o|$, and Miller indices revealed no trends which would explain the relatively poor R factor. In this study, 273 pairs of *hk*0 reflections were collected; the average agreement between pairs was 1.1 %, indicating that the data are of good quality. Presumably, the poor agreement is the fault of the model. The maximum density on a final difference Fourier map was 0.61 e/Å^3; all of the first 20 residual peaks were closely associated with the aromatic rings. This indicates that the rigid group approximation was not adequate, but the extra computing which would be necessary to describe fully the aromatic rings could not be justified.

The positional and thermal parameters for all atoms 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. Table 3 lists the idealized positional coordinates for all hydrogen atoms. A list presenting the values of $10|F_o|$ and $10|F_c|$ for all those reflections

BLE 1

SITIONAL AND ANISOTROPIC THERMAL PARAMETERS FOR $Ni(PTo_3)_2(PhN{=}NPh)$

m	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	−0.22682(8)	0.22644(5)	−0.22962(9)	58.2(10)	31.9(4)	73.0(12)	3.9(5)	27.5(8)	17.3(5)
1)	−0.17727(14)	0.20211(9)	−0.04065(15)	66.7(16)	33.8(6)	70.8(18)	8.3(8)	31.6(14)	16.4(8)
2)	−0.05924(14)	0.29482(9)	−0.21618(16)	62.4(16)	32.4(7)	84.9(20)	3.1(8)	33.4(14)	18.3(9)
1)	−0.4040(4)	0.1876(4)	−0.3332(5)	61(5)	34(2)	84(6)	1(2)	31(5)	16(3)
2)	−0.3542(4)	0.2152(3)	−0.4036(5)	60(5)	36(2)	73(6)	1(2)	24(6)	20(3)
37)	−0.4197(9)	−0.1158(5)	−0.0131(10)	228(14)	39(4)	253(16)	14(5)	151(13)	47(6)
47)	0.3547(7)	0.1689(6)	0.3307(8)	76(8)	108(6)	146(11)	44(6)	− 6(8)	15(7)
67)	−0.3756(9)	0.4469(5)	0.1661(10)	182(13)	63(4)	219(15)	31(6)	124(12)	−2(6)
67)	−0.1351(7)	0.5790(4)	−0.4766(8)	163(11)	35(3)	151(11)	17(4)	67(8)	36(5)
77)	0.3897(8)	0.4299(6)	0.3109(8)	101(9)	100(6)	116(11)	− 12(6)	10(8)	−7(6)
87)	0.1179(10)	0.1057(5)	−0.5261(10)	280(17)	62(4)	248(17)	73(7)	194(15)	47(7)

Group	x_c^c	y_c	z_c	δ	ε	η
Ring 1	0.4616(3)	0.2868(2)	−0.2761(3)	−0.207(4)	2.388(3)	2.281(4)
Ring 2	−0.3142(3)	0.0975(2)	−0.5455(3)	−0.454(4)	2.501(3)	−1.120(4)
Ring 3	−0.3047(3)	0.0352(2)	−0.0237(3)	−1.685(3)	−2.302(3)	0.441(4)
Ring 4	0.1035(3)	0.1899(2)	0.1555(3)	3.004(3)	2.370(3)	2.851(4)
Ring 5	−0.2725(3)	0.3312(2)	0.0792(3)	−0.058(4)	2.269(2)	1.988(4)
Ring 6	−0.1007(2)	0.4464(1)	−0.3478(2)	−1.343(2)	−3.006(3)	−2.663(3)
Ring 7	0.1795(3)	0.3667(2)	0.0580(3)	−2.501(3)	2.647(3)	2.394(3)
Ring 8	0.0389(3)	0.1962(2)	−0.3745(3)	−0.142(3)	2.582(2)	−1.193(3)

[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 value of β have been multiplied by 10^4.

[c] These quantities have been defined previously[22].

used in refinement of the structure is available*.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure consists of the packing of discrete molecules. The gross features of the structure are determined by intra- and inter-molecular packing. Figure 1 presents the numbering scheme for the more important atoms of the structure. Only the six α carbon atoms of the phosphines are presented for sake of clarity The numbering for all rings starts at the α carbon and works around the ring, numbering the tolyl methyl carbon atoms last. Hydrogen atoms have the same number as the carbon atoms to which they are attached, with 1, 2, or 3 to indicate the three methyl

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(*continued on p.* 397)

TABLE 2

POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR PHENYL AND TOLYL RING CARBON ATOMS

Atom	*x*	*y*	*z*	*B*(Å^2)
C(11)	−0.4692(4)	0.2402(2)	−0.3049(4)	3.5(1)
C(12)	−0.5208(4)	0.2173(2)	−0.2310(4)	4.8(1)
C(13)	−0.5899(5)	0.2639(2)	−0.2022(5)	6.0(2)
C(14)	−0.6075(4)	0.3334(3)	−0.2473(5)	6.2(2)
C(15)	−0.5560(5)	0.3564(2)	−0.3212(5)	6.1(2)
C(16)	−0.4869(4)	0.3097(2)	−0.3500(4)	5.0(2)
C(21)	−0.3344(4)	0.1540(2)	−0.4728(4)	3.6(1)
C(22)	−0.3640(4)	0.0757(2)	−0.4697(3)	4.4(1)
C(23)	−0.3436(5)	0.0191(2)	−0.5423(4)	5.4(2)
C(24)	−0.2939(5)	0.0410(2)	−0.6181(4)	6.3(2)
C(25)	−0.2644(5)	0.1193(3)	−0.6213(4)	5.8(2)
C(26)	−0.2847(4)	0.1758(2)	−0.5486(4)	4.8(1)
C(31)	−0.2502(3)	0.1077(2)	−0.0291(4)	3.5(1)
C(32)	−0.3522(4)	0.0623(2)	−0.1380(3)	3.8(1)
C(33)	−0.4066(3)	−0.0102(2)	−0.1327(3)	4.8(2)
C(34)	−0.3591(4)	−0.0374(2)	−0.0184(4)	5.0(2)
C(35)	−0.2571(4)	0.0080(2)	0.0904(3)	5.3(2)
C(36)	−0.2027(4)	0.0806(2)	0.0851(3)	5.0(2)
C(41)	−0.0164(3)	0.1996(2)	0.0717(3)	3.4(1)
C(42)	0.0546(4)	0.2495(2)	0.1885(4)	4.2(1)
C(43)	0.1754(4)	0.2398(2)	0.2723(3)	5.2(2)
C(44)	0.2234(3)	0.1802(3)	0.2393(4)	5.4(2)
C(45)	0.1523(3)	0.1303(2)	0.1225(4)	5.4(2)
C(46)	0.0325(4)	0.1400(2)	0.0387(3)	4.4(1)
C(51)	−0.2251(4)	0.2753(2)	0.0356(4)	3.6(1)
C(52)	−0.2530(5)	0.2640(2)	0.1314(4)	5.4(2)
C(53)	−0.3003(5)	0.3200(3)	0.1751(4)	6.0(2)
C(54)	−0.3198(5)	0.3871(2)	0.1229(5)	5.5(2)
C(55)	−0.2919(5)	0.3984(2)	0.0271(4)	5.1(2)
C(56)	−0.2446(4)	0.3424(2)	−0.0166(4)	4.1(1)
C(61)	−0.0825(3)	0.3828(1)	−0.2863(3)	3.2(1)
C(62)	−0.2003(3)	0.3850(2)	−0.3851(4)	3.7(1)
C(63)	−0.2185(3)	0.4486(2)	−0.4467(3)	4.6(1)
C(64)	−0.1188(4)	0.5100(2)	−0.4094(4)	4.3(1)
C(65)	−0.0010(3)	0.5078(2)	−0.3106(4)	4.4(1)
C(66)	0.0172(3)	0.4443(1)	−0.2490(3)	4.1(1)
C(71)	0.0779(3)	0.3353(2)	−0.0617(3)	3.7(1)
C(72)	0.0695(3)	0.3953(2)	0.0156(4)	4.5(1)
C(73)	0.1710(4)	0.4267(2)	0.1353(4)	5.3(2)
C(74)	0.2811(4)	0.3981(3)	0.1778(3)	5.6(2)
C(75)	0.2896(3)	0.3381(3)	0.1005(4)	5.7(2)
C(76)	0.1880(4)	−0.193(3)	−0.0193(3)	4.9(2)
C(81)	0.0004(4)	0.2405(2)	−0.3035(4)	3.5(1)
C(82)	0.0062(5)	0.1629(2)	−0.2930(4)	4.8(1)
C(83)	0.0446(5)	0.1186(2)	−0.3541(5)	5.8(2)
C(84)	0.0774(5)	0.1519(3)	−0.4456(4)	5.6(2)
C(85)	0.0716(5)	0.2294(2)	−0.4561(4)	5.9(2)
C(86)	0.0332(5)	0.2737(2)	−0.3850(4)	5.2(2)

TABLE 3

IDEALIZED POSITIONAL COORDINATES FOR HYDROGEN ATOMS[a]

Atom	*x*	*y*	*z*	*Atom*	*x*	*y*	*z*
H(12)	0.491	0.167	−0.199	H(55)	−0.306	0.446	−0.011
H(13)	0.373	0.248	−0.149	H(56)	−0.224	0.350	−0.085
H(14)	0.344	0.367	−0.225	H(57-1)	−0.470	0.441	−0.165
H(15)	0.432	0.407	−0.352	H(57-2)	−0.336	0.502	−0.101
H(16)	0.550	0.327	−0.402	H(57-3)	−0.362	0.443	−0.016
H(22)	−0.400	0.060	−0.416	H(62)	−0.272	0.341	−0.413
H(23)	−0.365	−0.037	−0.540	H(63)	−0.303	0.450	−0.518
H(24)	−0.280	−0.000	−0.670	H(65)	0.070	0.552	−0.284
H(25)	−0.228	0.134	−0.675	H(66)	0.101	0.443	−0.178
H(26)	−0.263	0.231	−0.551	H(67-1)	−0.183	0.564	−0.571
H(32)	−0.387	0.082	−0.220	H(67-2)	−0.051	0.613	−0.453
H(33)	−0.480	−0.043	−0.211	H(67-3)	−0.183	0.616	−0.453
H(35)	−0.223	−0.012	0.172	H(72)	−0.009	0.416	−0.014
H(36)	−0.129	0.113	0.162	H(73)	0.165	0.470	0.191
H(37-1)	−0.410	−0.161	−0.065	H(75)	0.369	0.318	0.132
H(37-2)	−0.378	−0.128	0.079	H(76)	0.195	0.264	−0.074
H(37-3)	−0.513	−0.121	−0.044	H(77-1)	0.474	0.442	0.313
H(42)	0.019	0.292	0.212	H(77-2)	0.380	0.481	0.351
H(43)	0.226	0.276	0.356	H(77-3)	0.400	0.392	0.373
H(45)	0.187	0.088	0.099	H(82)	−0.017	0.139	−0.234
H(46)	−0.019	0.104	−0.044	H(83)	0.050	0.063	−0.356
H(47-1)	0.410	0.166	0.289	H(85)	0.096	0.253	−0.514
H(47-2)	0.403	0.212	0.408	H(86)	0.030	0.329	−0.392
H(47-3)	0.353	0.117	0.366	H(87-1)	0.213	0.117	−0.490
H(52)	−0.239	0.216	0.169	H(87-2)	0.093	0.046	−0.535
H(53)	−0.320	0.312	0.244	H(87-3)	0.080	0.117	−0.616

[a] A C–H distance of 1.00 Å and for the methyl carbon atoms a tetrahedral geometry was assumed. The number of the hydrogen atom indicates the carbon atom to which it is attached.

TABLE 4

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	*Minimum*	*Intermediate*	*Maximum*
Ni	0.180(2)	0.187(2)	0.243(1)
P(1)	0.188(3)	0.198(2)	0.236(2)
P(2)	0.179(3)	0.202(3)	0.250(2)
N(1)	0.180(8)	0.207(8)	0.251(7)
N(2)	0.176(8)	0.187(8)	0'268(7)
C(37)	0.199(12)	0.341(11)	0.390(12)
C(47)	0.167(13)	0.351(12)	0.422(12)
C(57)	0.242(12)	0.331(11)	0.376(12)
C(67)	0.196(11)	0.298(10)	0.330(10)
C(77)	0.205(12)	0.335(12)	0'411(12)
C(87)	0.236(12)	0.302(12)	0.432(13)

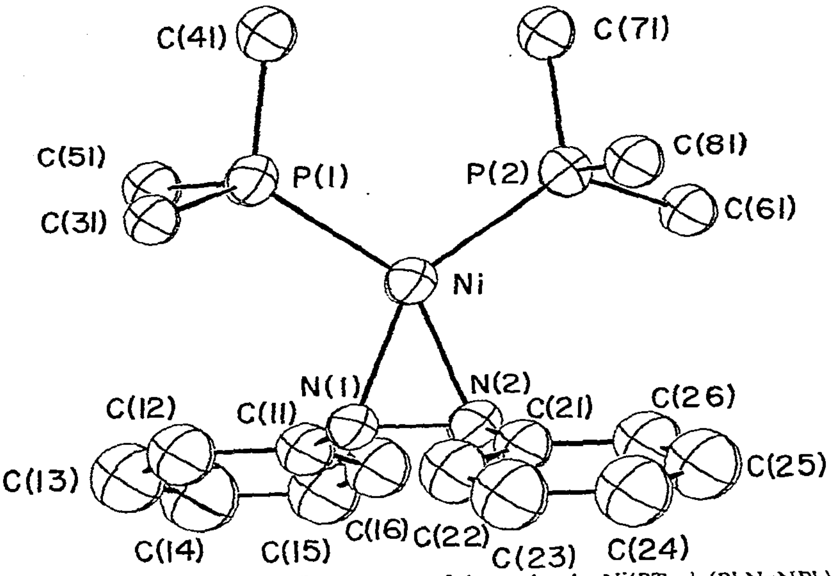

Fig. 1. The structurally significant atoms of the molecule, Ni(PTo$_3$)$_2$(PhN=NPh), showing the labeling scheme. The 50% probability ellipsoids of thermal vibration are shown.

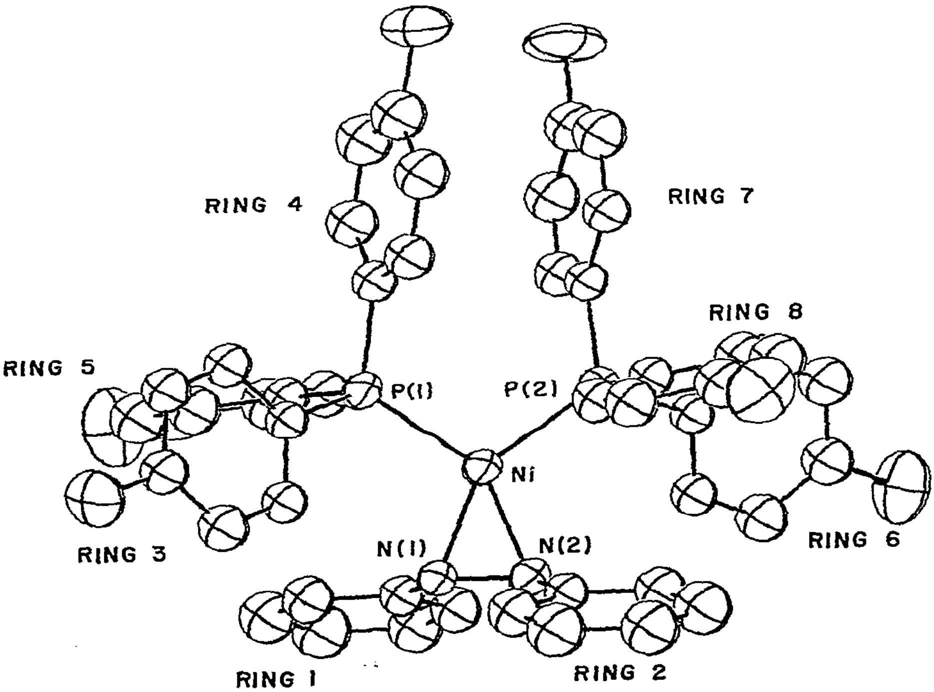

Fig. 2. The Ni(PTo$_3$)$_2$(PhN=NPh) molecule with H atoms omitted for the sake of clarity. Labeling scheme for rings is shown, as are the 50% probability ellipsoids of thermal vibration.

hydrogens on each tolyl ring. Figures 1 and 2 display the 50% probability ellipsoids for thermal motion. The root-mean-square amplitudes of vibration are listed in Table 4. The complete molecule with the numbering scheme for the tolyl rings is shown in Fig. 2. The packing of the rings is graphitic; that is, adjacent rings are roughly parallel with a separation of 4 Å. Intermolecular contacts are normal, the shortest being 1.99 Å between H(15) and H(57-1) of adjacent molecules.

Relevant interatomic distances and angles are presented in Tables 5 and 6. Table 7 presents data on various dihedral angles.

As in the previous structure of $Ni[(CH_3)_3C{-}N{\equiv}C]_2(PhN{=}NPh)$, the molecule possesses essentially C_2 symmetry, but in this case, the deviations are somewhat greater. The nickel atom is three coordinate, if the azobenzene is regarded as a monodentate ligand. The inner coordination is nearly planar with a small dihedral angle of 7.6(3)° between the NiP(1)P(2) and NiN(1)N(2) planes. This near planarity is also reflected in the small deviations of these atoms from a least-squares plane (Table 8) through them, the greatest deviation being 0.142(5) Å for N(1).

The Ni–P distances for P(1) and P(2) are 2.195(3) and 2.201(3) Å, respectively. The two Ni–N distances for N(1) and N(2) are 1.932(5) and 1.927(5) Å. This is the first structural indication that the bonding between the nickel atom and the azobenzene, as indicated by the usual description of π-bonding to transition metals, is not as great as in the t-butyl isocyanide complex where the Ni–N distance is 1.898(4) Å. The bond angles around the nickel atom are: P(1)NiP(2), 107.4(1)°; N(1)NiN(2), 41.6(2)°; P(1)NiN(1), 105.9(2)°; and P(2)NiN(2), 105.2(2)°. The variations in the phosphorus–carbon distances and also in the distances from the *para*-carbon atoms to the methyl-carbon atoms are statistical, with average values of 1.834(6) Å and 1.521(15) Å, respectively. The variations in the NiPC(n1) angle where $n=3,4,5$ for P(1) and $n=6,7,8$ for P(2) may be attributed to intramolecular packing but are probably of little significance in this structure.

As would be expected, the N–N distance has lengthened from the 1.24(3) Å of free azobenzene[18]* to 1.371(6) Å. This is comparable with the value of 1.385(5) Å in the previous t-butyl isocyanide structure, and the errors on these distances make it impossible to draw any conclusions. The N(1)C(11) and N(2)C(21) distances are 1.427(8) Å and 1.423(8) Å respectively; values similar to those in free azobenzene, 1.433 Å, and the previous structure, 1.423(5) Å.

The structure of the coordinated azobenzene is unusual in that it may be described as two planes intersecting along the N(1)N(2) axis. The two phenyl groups are bent back, away from the nickel atom. This is indicated by the dihedral angle of 23.5(3)° between the C(11)N(1)N(2) and C(21)N(2)N(1) planes. This angle is 0° by symmetry in free azobenzene and has increased to 26.8(4)° in the isocyanide structure. This is another indication that the nickel–N=N interaction is not as strong in the present structure as in the previous one. Unlike either free azobenzene or the coordinated azobenzene of the previous structure, there is only a very slight rotation about the N–C bonds as indicated by the dihedral angles: C(11)N(1)N(2)–C(11)C(13)-C(15), 3.0(4)°; and C(21)N(2)N(1)–C(21)C(25)C(23), 1.0(3)°. These angles were 14.3(4)° and 13.9(4)° in the isocyanide structure and both were 17.1° in the uncoor-

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* Note that in this reference there are two molecules of azobenzene per asymmetric unit, but we have disregarded the dimensions of the one which is disordered.

(*continued on* p. 400)

TABLE 5

SELECTED DISTANCES (Å) IN $Ni(PTo_3)_2(PhN{=}NPh)$

Bond distances			*Non-bonded distances*		
Ni–P(1)	2.195(3)	2.198(3)[a]	P(1)–N(1)	3.298(5)	3.291(7)
Ni–P(2)	2.201(3)		P(2)–N(2)	3.284(5)	
Ni–N(1)	1.932(5)	1.930(5)	P(1)–P(2)	3.543(4)	
Ni–N(2)	1.927(5)		N(1)–C(17)	2.493(7)	2.490(7)
N(1)–N(2)	1.371(6)		N(2)–C(22)	2.486(7)	
N(1)–C(11)	1.427(8)	1.425(8)	N(1)–C(12)	2.394(9)	2.395(9)
N(2)–C(21)	1.423(8)		N(2)–C(26)	2.395(9)	
P(1)–C(31)	1.848(4)	1.834(6)	N(1)–C(22)	2.704(8)	2.717(12)
P(1)–C(41)	1.823(4)		N(2)–C(16)	2.729(8)	
P(1)–C(51)	1.836(6)		N(1)–C(21)	2.311(9)	2.317(9)
P(2)–C(61)	1.840(4)		N(2)–C(11)	2.323(9)	
P(2)–C(71)	1.832(4)				
P(2)–C(81)	1.827(6)				
C(34)–C(37)	1.514(10)	1.521(15)			
C(44)–C(47)	1.533(9)				
C(54)–C(57)	1.514(13)				
C(64)–C(67)	1.520(9)				
C(74)–C(77)	1.526(8)				
C(84)–C(87)	1.518(15)				

[a] These are average quantities. The estimated standard deviation in parentheses is the larger of an individual standard deviation or of the standard deviation of a single observation as calculated from the mean.

TABLE 6

SELECTED INTRAMOLECULAR BOND ANGLES (Deg.) IN $Ni(PTo_3)_2(PhN{=}NPh)$

P(1)NiP(2)	107.4(1)	
N(1)NiN(2)	41.6(2)	
P(1)NiN(1)	105.9(2)	105.6(4)
P(2)NiN(2)	105.2(2)	
NiN(1)N(2)	69.0(3)	69.2(3)
NiN(2)N(1)	69.4(3)	
NiN(1)C(11)	109.5(2)	108.0(15)
NiN(2)C(21)	106.5(3)	
N(1)C(11)C(12)	116.0(4)	116.2(4)
N(2)C(21)C(26)	116.3(4)	
N(1)C(11)C(16)	123.9(6)	123.8(6)
N(2)C(21)C(22)	123.7(5)	
N(1)N(2)C(21)	111.6(5)	111.9(5)
N(2)N(1)C(11)	112.2(5)	
NiP(1)C(31)	118.1(1)	115.6(2.1)
NiP(1)C(41)	120.2(2)	
NiP(1)C(51)	107.6(2)	
NiP(2)C(61)	115.2(2)	
NiP(2)C(71)	120.5(2)	
NiP(2)C(81)	111.9(2)	

TABLE 7

SELECTED INTRAPLANAR AND VECTOR-PLANE-NORMAL ANGLES (Deg) IN $Ni(PTo_3)_2$-(PhN=NPh)

Dihedral angles[a]		*Vector-plane-normal angles*[b]	
P(1)NiP(2)–N(2)NiN(1)	−7.6(3)	N(1)N(2)–NiP(1)P(2)	96.9(3)
P(2)NiN(2)–N(1)NiP(1)	5.6(2)	N(1)N(2)–C(11)C(13)C(15)	91.3(3)
C(11)N(1)N(2)–C(21)N(2)N(1)	23.5(3)	N(1)C(11)–C(11)C(13)C(15)	91.9(3)
C(11)C(13)C(15)–C(11)N(1)N(2)	−3.0(4)	N(2)C(21)–C(21)C(23)C(25)	89.0(3)
NiN(1)N(2)–N(1)N(2)C(11)	−103.2(3)	C(11)N(1)–NiN(1)N(2)	−25.7(4)
C(21)C(25)C(23)–C(21)N(2)N(1)	−1.0(3)	C(21)N(1)–NiN(1)N(2)	−156.2(4)
NiN(1)N(2)–N(1)N(2)C(21)	100.3(3)	N(1)N(2)–C(21)C(23)C(25)	89.7(3)
C(11)C(13)C(15)–C(21)C(25)C(23)	27.1(2)		

[a] Let the two groups of atoms be A(1)A(2)A(3) and B(1)B(2)B(3). Form vector *V*(1) from A(1) to A(2). Form vector *V*(2) from A(1) to A(3). Then the normal to the plane of A(1)A(2)A(3) is parallel to *V*(1) × *V*(2). Form a similar normal to the plane of B(1)B(2)B(3). Then the dihedral angle is defined as the angle between these two normals. The dihedral angle of planes which have two defining points, 2 and 3, in common is equal to the torsional angle of the chain of atoms 1,2,3,4.

[b] Let the two groups of atoms be A(1)A(2) and B(1)B(2)B(3). Form the vector *V*(1) from A(1) to A(2). Form the normal *V*(2) to B(1)B(2)B(3) as for the dihedral angles. Then the angle given here is between *V*(1) and *V*(2).

TABLE 8

DEVIATIONS (Å) FROM WEIGHTED LEAST-SQUARES PLANES OF ATOMS USED TO DETERMINE THE PLANES[a]

Atom	*Plane 1*	*Plane 2*	*Plane 3*
Ni	0.011(1)		
P(1)	−0.006(2)		
P(2)	−0.014(2)		
N(1)	−0.142(5)	−0.026(4)	−0.008(4)
N(2)	−0.020(5)	0.008(4)	−0.005(4)
C(11)		0.012(3)	
C(12)		0.010(4)	
C(13)		−0.000(4)	
C(14)		−0.008(4)	
C(15)		−0.005(4)	
C(16)		0.004(4)	
C(21)			0.010(4)
C(22)			0.006(3)
C(23)			−0.003(4)
C(24)			−0.008(4)
C(25)			−0.005(4)
C(26)			0.004(4)

Plane No.	*A*	*B*	*C*	*D*
1	6.511	−15.563	−3.804	−4.139
2	5.637	4.850	5.425	−3.163
3	7.980	− 2.776	4.511	−5.239

[a] Plane equation: $Ax+By+Cz-D=0$ with *x*, *y*, *z* in triclinic coordinates, *A*, *B*, *C*, *D* in Å.

dinated azobenzene. This planarity is reflected in the fact that the largest deviation from a least-squares plane through phenyl ring 1 and the two nitrogen atoms is −0.026(4) Å for N(1). For the corresponding plane through phenyl ring 2, the largest deviation is 0.010(4) Å for C(21). This unusual deviation from other structures is probably a result of the packing of the various aromatic rings and thus bears little direct relation to the nature of the metal–azobenzene π bond.

Though there is no rotation about the two N–C bonds, there is a distortion indicated by the angles N(1)C(11)C(12), 116.0(4)° and N(1)C(11)C(16), 123.9(6)° for the N(1)C(11) bond and N(2)C(21)C(26), 116.3(4)°, and N(2)C(21)C(22), 123.7(5)° for N(2)C(21). As in the previous structures where the same effects were observed, this may be attributed to steric strain resulting from non-bonded interactions of the *ortho* hydrogen atoms of the phenyl rings with the opposite azobenzene nitrogen atoms. These rather short non-bonded distances of 2.704(8) Å for N(1)C(22) and 2.729(8) Å for N(2)C(16) may be compared with the corresponding values of 2.746(6) Å and 2.723(6) Å for the isocyanide complex.

The cyanide stretching frequencies of a number of compounds $Ni[(CH_3)_3C–N{\equiv}C]_2L$, prepared by Otsuka *et al.*[19], are presented in Table 9. If one accepts the procedure of Cook *et al.*[20] in assigning degrees of electron transfer to the extremes of

TABLE 9

ISOCYANIDE STRETCHING FREQUENCIES[a] OF A SERIES OF COMPOUNDS, $Ni[(CH_3)_3C–N{\equiv}C]_2L$

L	$\nu(N{\equiv}C)$ *(cm⁻¹)*
$[(CH_3)_3C–N{\equiv}C]_2$	2000
$[PhC{\equiv}CPh]$	2138
$[PhN{=}NPh]$	2168
$[(NC)_2C{=}C(CN)_2]$	2194
$[I]_2$	2194
$[O_2]$	2196

[a] From ref. 19.

TABLE 10

THE VISIBLE ABSORPTION BANDS OF VARIOUS AZOBENZENE SPECIES

	λ_{max} *(nm)*
$NiL_2(PhN{=}NPh)$	
$L = P(C_6H_5)_3$	526
$L = P(C_6H_4CH_3)_3$	523
$L = P(C_6H_5)_2(C_2H_5)$	505
$L = P(C_6H_5)(C_2H_5)_2$	500
$L = P(CH_3)_3$	489
$L = P(C_4H_9)_3$	482
$L = (CH_3)_3C–N{\equiv}C$	465
$PhN{=}NPh$	440
$Li^+(PhN{=}NPh)^-$ [a]	605
$(Li^+)_2(PhN{=}Nph)^{2-}$ [a]	380

[a] From ref. 21.

a series, then nickel would have a formal oxidation state of 2 in the diiodo complex and 0 in the tetrakis(t-butylisocyanide) complex. The cyanide stretching frequency is then an indication of the number of electrons transferred from nickel to L. The range of stretching frequencies could have been expanded by going to basic phosphines on the lower end and to the chloride on the upper end, but one may still conclude that between one and two electrons have been transferred to azobenzene in the azobenzene complex.

This observation is consistent with the visible absorption data for a series of nickel azobenzene complexes given in Table 10. Only the lowest, presumably the $n \rightarrow \pi^*$, transition was used because of interference of other bands at higher energy. The spectra of azobenzene, its monoanion and its dianion have been determined previously[21]. In the complex $Ni(L)_2(PhN{=}NPh)$ as the basicity of the ligands, L, about the nickel increases, more electron density would be donated through the nickel to the azobenzene. It has already been argued that between one and two electrons have been transferred to the azobenzene. One would therefore expect the shift in λ_{max} to be to shorter wavelength with increasing basicity. This is the trend observed. Though they are not directly comparable because of varying degrees of σ-forward and π-back bonding for the two types of ligands, the λ_{max} values of 523 nm and 465 nm for $L = PTo_3$ and $(CH_3)_3C{-}N{\equiv}C$, respectively, indicate that more electron density is transferred to azobenzene when $L = (CH_3)_3C{-}N{\equiv}C$. This conclusion is consistent with the related structural effects which have been discussed.

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