STEREOCHEMISTRY AND BONDING IN NICKEL—OLEFIN COMPLEXES:

THE STRUCTURE OF TETRAMETHYLETHYLENENICKEL 1,2-BIS-(DICYCLOHEXYLPHOSPHINO)ETHANE

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Summary

The structure of tetramethylethylenenickel 1,2-bis(dicyclohexylphosphino)ethane, $(CH_3)_2C_2(CH_3)_2Ni[(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2]$, has been determined from 4995 observed, absorption-corrected reflections collected by counter methods. The compound crystallizes in the monoclinic space group $C_{2h}^5 - P2_1/n$ with cell dimensions a 17.1306(7), b 16.9016(7), c 11.4899(8) Å and β 100.082(5)°. The calculated density is 1.147 g/cm³ for $Z = 4$. Least-squares refinement yielded a final conventional R value of 0.036. If one coordination site is assigned to the olefin, the nickel atom is three-coordinate. Although no crystallographic symmetry is required, the molecule posses idealized C_2 symmetry. The average Ni—C and Ni—P bond lengths are 1.981(2) and 2.156(6) Å, respectively. The central bond of the olefin has been lengthened upon coordination to 1.421(3) Å. The tetramethylethylene moiety is distorted from planarity with the $C(CH_3)_2$ planes bent away from the nickel atom by 27.2(6)°. The nickel atom and four atoms bonded to it are not coplanar, the central bond of the tetramethylethylene species forming a 16.5° angle with the Ni,P(1),P(2) plane. A segmented rigid-body analysis of the thermal motion of the molecule indicates that the barrier to rotation of the olefin is 18 kcal/mole.

Introduction

Compounds with the general formula $(olefin)_xNiL_{3-x}$ ($x = 1—3$ and $L =$ phosphine) have been intensively studied in this laboratory [1]. Using $L = P(C_6H_{11})_3$, Jonas has shown that the reaction olefin + $NiL_2 \rightarrow (olefin)NiL_2$ is not possible when the olefin is tetramethylethylene (TME), although the ethylene complex is formed without difficulty. However, when the chelate phosphine ligand $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$ (TCDP) was bonded to the nickel atom, the complex (TME)Ni(TCDP) could be isolated. Ligand competition experiments

have shown that ethylene forms more stable complexes with Ni(TCDP) than does TME [2].

Recently a number of structural investigations of transition metal—olefin complexes have been reported. The most precise measurements of the conformation of the coordinated olefins have been determined when the olefin is substituted with four functional groups such as CN, F or Cl [3], since the precision of the positions of hydrogen atoms are generally an order of magnitude less than those of larger atoms (such as carbon atoms) in X-ray structural analysis. Invariably an olefin substituted with CN, F or Cl forms a more stable complex than does ethylene with a given transition element—ligand system. Upon complex formation with a transition metal, the olefins distort from planarity in such a way that the four substituents are bent away from the metal atom. The extent of this distortion has been used to indicate both the mode and strength of the metal—olefin interaction [3]. In order to test these ideas, it was of interest to determine the stereochemistry of a complex containing an olefin which forms a weaker bond to the transition metal than does ethylene.

(TME)Ni(TCDP) is an excellent compound for such a study. In addition to being able to observe the stereochemistry of the complexed olefin precisely, we hoped to be able to compare the Ni—C(olefin) and Ni—P distances with those found in other Ni^0 structures reported from this laboratory and elsewhere.

Experimental

Yellow crystals of (TME)Ni(TCDP) were provided by Dr. K. Jonas of this Institute. A crystal with well developed faces was mounted under argon in a glass capillary. Space group information and preliminary unit cell constants were obtained from Weissenberg and precession photographs. The crystal was then transferred to a PDP-8/s automated Siemens diffractometer with b^* aligned along the φ-axis. Eighty-nine 2θ maxima (Cu-$K_{\bar{\alpha}}$ or Cu-K_{α_1} and Cu-K_{α_2}) of a number of high angle reflections were measured; these measurements were used to refine the unit cell constants and to generate an accurate orientation matrix for data collection. Crystal data are given in Table 1. ω scans of several strong, low angle reflections indicated that the crystal quality was satisfactory.

Intensity data (hkl, $\bar{h}kl$, $2\theta \leqslant 134°$, Cu-K_α) were measured by the θ-2θ scan technique using the five value method. A scan speed (20°, 10° or 5° (2θ/

TABLE 1

CRYSTAL DATA

Formula	$C_{32}H_{60}NiP_2$		t	20°C
Mol. wt.	565.49		Z	4
Color yellow			d_c	1.147 g cm^{-3}
Monoclinic			μ(Cu-$K_{\bar{\alpha}}$)·	18.4 cm^{-1}
a	17.1306(7)^a Å		Absences:	$h0l$, $h+l = 2n+1$
b	16.9016(7)			$0k0$, $k = 2n+1$
c	11.4899(8)		Space group	$P2_1/n$
β	100.082(5)°			

^{a} A number in parentheses following a numerical value here and throughout the paper is the estimated standard deviation in the last digit.

min) and one of six attenuators were automatically chosen by the computer for each reflection in order to keep the net number of counts constant for each data point. The symmetrical scan range, 1.20—2.40° (2θ), was derived from a function of the Bragg angle. In order to check on the stability of the diffractometer system as well as the alignment of the crystal, one reflection (400) was remeasured after collection of 40 intensities. This measurement was made with and without an occulator inserted in the lower half of the counter window. During data collection the intensity of the 400 reflection varied only slightly. A total of 5839 independent reflections was collected.

The distances between the six crystal faces were measured, and the faces were indexed. The intensities were reduced to structure factors applying the usual corrections for Lorenz and polarization effects as well as absorption. The transmission factor varied from 0.51 to 0.66. The condition $I > 3\sigma(I)$ was met by 4995 reflections, which were deemed to be "observed". The relative weight, w, of each "observed" reflection was taken as the reciprocal of its variance, as calculated with p 0.04 [4]. "Unobserved" reflections were assigned zero weights.

The structure was solved by the heavy atom method. The positions of the nickel and two phosphorus atoms were derived from a 3-dimensional sharpened Patterson function. A subsequent electron density map revealed the 32 carbon atoms.

The structure was refined by least-squares methods. The function minimized was $\Sigma w \Delta^2$, $\Delta = \left| |F_o| - |F_c| \right|$. Neutral isolated atom scattering factors [5] were used for all atoms except H [6]. The real and imaginary parts of the anomalous scattering factors for Ni and P [7] were applied to the calculated structure factors. The discrepancy indices are defined as $R_1 = \Sigma \Delta / \Sigma |F_o|$ and $R_2 = [\Sigma w \Delta^2 / \Sigma w |F_o|^2]^{1/2}$. Isotropic least-squares refinement converged with R_1 0.112 and R_2 0.167.

All hydrogen atoms of the TCDP ligand were placed in idealized positions: C—H 1.00 Å, H—C—H 109.5°, the CH_2 plane set perpendicular to the relevant C_3 or PC_2 plane. These calculated positions were confirmed on a difference Fourier map. This map was also used to locate the positions of the methyl hydrogen atoms. The non-hydrogen atoms were assigned anisotropic temperature factors, and the hydrogen atoms were refined isotropically. Due to the large number of parameters, further refinement was done with the atoms grouped into four large blocks: Ni,P(1),P(2),C(1)-C(23); Ni,P(1),P(2),C(24)-C(46); H(1A)-H(22B); H(23A)-H(46B). In addition, an extinction parameter was refined [8], the path length for each reflection being given the arbitrary value of 1 cm. The scale factor and extinction parameter were included in the first two blocks. Refinement of the 557 parameters was ended when the maximum value of shift/error was 0.2. The final values of R_1 were 0.033 (excluding "unobserved" data) and 0.036 (all data); R_2 was 0.053. The goodness of fit was 2.15. Plots of $w\Delta^2$ versus $|F_o|$, $\sin\theta/\lambda$ and the Miller indices did not show any particular trends. The final value of the extinction parameter was 44(15), and the largest correction to $|F_c|$ was calculated for the 101 reflection, 16%. The final positional and thermal parameters are given in Table 2, the estimated standard deviations being calculated from the diagonal elements of the inverse of the least-squares matrix. Our numbering scheme for the non-hydrogen atoms is defined by Fig. 1. The hydrogen atoms are numbered after the atom to which they are attached. Selected bond distances and angles are given in Tables 3 and 4, respectively.

TABLE 2

POSITIONAL ($\times 10^4$) AND THERMAL ($\times 10^3$) PARAMETERS FOR (TME)Ni(TCDP)

(a) Non-hydrogen atoms

Atom	x	y	z	U_{11}^a	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Ni	1492.7(2)	1860.0(2)	2209.9(3)	38.8(2)	42.7(2)	43.0(2)	−4.1(1)	0.9(1)	9.9(1)
P(1)	2590.7(3)	2485.6(3)	2249.7(4)	35.2(2)	42.0(3)	46.2(3)	−1.8(2)	0.4(2)	13.6(2)
P(2)	1221.5(3)	2533.6(3)	3685.9(4)	41.6(3)	48.1(3)	42.9(3)	−2.6(2)	1.9(2)	16.1(2)
C(1)	961(2)	235(2)	2505(3)	147(3)	63(2)	89(2)	−38(2)	2(1)	36(2)
C(2)	765(1)	965(1)	1709(2)	63(1)	67(1)	66(1)	−25(1)	−10(1)	11(1)
C(3)	1259(1)	1116(1)	862(2)	60(1)	54(1)	54(1)	−10(1)	−8(1)	5(1)
C(4)	1897(2)	550(2)	644(3)	88(2)	67(2)	95(2)	−2(1)	−28(1)	20(2)
C(5)	−112(2)	1147(2)	1462(3)	62(2)	67(2)	126(3)	−40(2)	−43(2)	21(2)
C(6)	904(2)	1649(2)	−259(2)	94(2)	92(2)	55(1)	−14(2)	2(1)	−4(1)
C(7)	2747(1)	3117(1)	3597(2)	47(1)	57(1)	62(1)	−10(1)	−12(1)	17(1)
C(8)	1970(1)	3336(1)	3991(2)	54(1)	56(1)	58(1)	−10(1)	−10(1)	20(1)
C(11)	3488(1)	1849(1)	2488(2)	38(1)	47(1)	47(1)	−1(1)	3(1)	13(1)
C(12)	4280(1)	2283(1)	2747(2)	38(1)	60(1)	74(1)	−4(1)	6(1)	13(1)
C(13)	4975(1)	1706(1)	2876(2)	39(1)	75(1)	66(1)	3(1)	4(1)	14(1)
C(14)	4919(1)	1074(1)	3793(2)	49(1)	76(2)	56(1)	13(1)	3(1)	7(1)
C(15)	4135(1)	643(1)	3531(2)	60(1)	61(1)	59(1)	9(1)	13(1)	15(1)
C(16)	3439(1)	1217(1)	3431(2)	45(1)	56(1)	53(1)	−0(1)	9(1)	13(1)
C(21)	2804(1)	3174(1)	1083(2)	40(1)	46(1)	59(1)	0(1)	7(1)	18(1)
C(22)	2116(1)	3762(1)	759(2)	52(1)	58(1)	78(2)	12(1)	19(1)	26(1)
C(23)	2252(1)	4315(1)	−238(2)	63(1)	61(1)	86(2)	13(1)	24(1)	23(1)
C(24)	2389(1)	3872(2)	−1314(2)	62(1)	83(2)	68(1)	−2(1)	28(1)	9(1)
C(25)	3084(1)	3299(2)	−1005(2)	72(2)	76(2)	63(1)	10(1)	17(1)	28(1)
C(26)	2963(1)	2739(1)	−9(2)	72(1)	58(1)	60(1)	12(1)	12(1)	31(1)
C(31)	269(1)	3096(1)	3459(2)	50(1)	54(1)	49(1)	4(1)	6(1)	17(1)
C(32)	118(1)	3505(1)	2255(2)	73(1)	67(1)	50(1)	11(1)	10(1)	15(1)
C(33)	−684(2)	3915(2)	2033(2)	81(2)	80(2)	63(1)	17(1)	7(1)	1(1)
C(34)	−782(1)	4482(1)	3018(2)	64(1)	64(1)	78(2)	14(1)	10(1)	13(1)
C(35)	−641(1)	4076(2)	4206(2)	72(2)	70(2)	75(2)	19(1)	10(1)	34(1)
C(36)	168(1)	3675(1)	4443(2)	71(1)	76(2)	48(1)	20(1)	6(1)	21(1)
C(41)	1228(1)	2092(1)	5170(2)	48(1)	57(1)	47(1)	8(1)	6(1)	17(1)
C(42)	1979(1)	1607(2)	5550(2)	55(1)	88(2)	64(1)	16(1)	20(1)	19(1)
C(43)	1976(2)	1189(2)	6728(2)	78(2)	113(2)	74(2)	35(2)	38(2)	20(1)
C(44)	1268(2)	686(2)	6705(3)	108(2)	80(2)	84(2)	33(2)	35(2)	49(2)
C(45)	514(2)	1167(2)	6356(2)	80(2)	80(2)	82(2)	8(1)	30(1)	41(1)
C(46)	497(1)	1586(2)	5186(2)	59(1)	80(2)	69(1)	0(1)	23(1)	24(1)

(b) Hydrogen atoms

Atom	x^b	y	z	U^c		Atom	x	y	z	U
H(1A)	75(2)	−26(2)	210(3)	114(10)		H(23A)	268(1)	464(1)	6(2)	97(9)
H(1B)	70(2)	25(2)	323(3)	121(12)		H(23B)	180(1)	464(1)	−44(2)	71(7)
H(1C)	159(2)	18(2)	282(3)	125(14)		H(24A)	191(1)	354(1)	−163(2)	65(6)
H(4A)	171(2)	13(2)	22(3)	127(12)		H(24B)	247(1)	422(1)	−193(2)	76(7)
H(4B)	210(2)	25(2)	142(3)	90(9)		H(25A)	359(1)	361(1)	−75(2)	79(8)
H(4C)	239(2)	84(2)	28(3)	107(10)		H(25B)	309(1)	299(1)	−175(2)	80(8)
H(5A)	−40(2)	72(2)	98(3)	129(12)		H(26A)	341(2)	240(1)	24(2)	74(7)
H(5B)	−34(2)	125(2)	203(3)	129(13)		H(26B)	249(1)	242(1)	−26(2)	60(6)
H(5C)	−16(2)	168(2)	101(3)	108(10)		H(31B)	−12(1)	268(1)	340(2)	54(6)
H(6A)	53(2)	124(2)	−75(3)	94(9)		H(32A)	55(1)	394(1)	226(2)	63(6)
H(6B)	136(2)	175(2)	−70(3)	86(9)		H(32B)	14(1)	311(1)	161(2)	53(6)
H(6C)	63(2)	199(2)	−6(3)	117(11)		H(33A)	−110(2)	355(1)	194(2)	116(10)
H(7A)	309(1)	282(2)	429(2)	79(8)		H(33B)	−73(1)	426(1)	130(2)	85(8)
H(7B)	310(2)	357(2)	345(2)	79(8)		H(34A)	−39(1)	492(1)	303(2)	82(8)
H(8A)	202(1)	352(1)	480(2)	68(7)		H(34B)	−136(1)	471(1)	283(2)	79(8)
H(8B)	175(2)	383(2)	346(3)	98(10)		H(35A)	−64(1)	447(1)	485(2)	71(7)
H(11B)	343(1)	157(1)	172(2)	53(6)		H(35B)	−110(1)	365(1)	416(2)	84(8)
H(12A)	432(1)	257(1)	351(2)	50(6)		H(36A)	23(1)	339(2)	517(2)	85(8)
H(12B)	435(1)	267(1)	206(2)	59(7)		H(36B)	57(1)	414(1)	445(2)	69(7)
H(13A)	543(2)	195(1)	306(2)	72(8)		H(41A)	125(2)	251(1)	567(2)	60(6)
H(13B)	494(1)	143(1)	215(2)	74(8)		H(42A)	246(1)	198(1)	564(2)	72(7)
H(14A)	496(1)	128(1)	461(2)	68(7)		H(42B)	197(1)	120(1)	492(2)	94(9)
H(14B)	539(1)	68(1)	393(2)	59(7)		H(43A)	203(1)	164(1)	734(2)	68(7)
H(15A)	407(1)	30(1)	413(2)	66(7)		H(43B)	246(1)	84(1)	689(2)	78(8)
H(15B)	408(1)	38(1)	274(2)	66(7)		H(44A)	132(1)	41(1)	750(2)	74(7)
H(16A)	345(1)	149(1)	422(2)	69(7)		H(44B)	131(1)	28(1)	608(2)	113(10)
H(16B)	295(1)	93(1)	318(2)	59(6)		H(45A)	46(1)	159(1)	701(2)	88(8)
H(21B)	327(1)	346(1)	137(2)	63(7)		H(45B)	4(1)	81(1)	617(2)	92(9)
H(22A)	198(1)	409(1)	145(2)	70(7)		H(46A)	5(2)	182(1)	494(2)	93(9)
H(22B)	165(1)	346(2)	48(2)	71(8)		H(46B)	48(1)	117(1)	456(2)	79(8)

^{a} The form of the anisotropic thermal ellipsoid is: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. ^{b} Positional parameters of H atoms have been multiplied by 10^3. ^{c} The U's of the H atoms have been multiplied by 10^3.

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TABLE 3

SELECTED BOND DISTANCES^a (Å) IN (TME)Ni(TCDP)

Ni—C(1)	1.980(2)	C(11)—C(12)	1.525(3)
Ni—C(3)	1.981(2)	C(12)—C(13)	1.527(3)
	——————	C(13)—C(14)	1.516(3)
av.	1.981(2)^b	C(14)—C(15)	1.512(3)
		C(15)—C(16)	1.527(3)
Ni—P(1)	2.152(1)	C(16)—C(11)	1.535(3)
Ni—P(2)	2.160(1)	C(21)—C(22)	1.538(3)
	——————	C(22)—C(23)	1.529(4)
av.	2.156(6)	C(23)—C(24)	1.499(4)
		C(24)—C(25)	1.529(4)
C(2)—C(3)	1.421(3)	C(25)—C(26)	1.528(3)
		C(26)—C(21)	1.520(3)
C(2)—C(1)	1.538(4)	C(31)—C(32)	1.529(3)
C(2)—C(5)	1.511(4)	C(32)—C(33)	1.520(4)
C(3)—C(4)	1.506(4)	C(33)—C(34)	1.515(4)
C(3)—C(6)	1.514(4)	C(34)—C(35)	1.509(4)
	——————	C(35)—C(36)	1.524(3)
av.	1.517(15)	C(36)—C(31)	1.527(3)
		C(41)—C(42)	1.524(3)
P(1)—C(7)	1.860(2)	C(42)—C(43)	1.529(4)
P(1)—C(11)	1.857(2)	C(43)—C(44)	1.477(4)
P(1)—C(21)	1.859(2)	C(44)—C(45)	1.520(4)
P(2)—C(8)	1.858(2)	C(45)—C(46)	1.517(4)
P(2)—C(31)	1.867(2)	C(46)—C(41)	1.519(3)
P(2)—C(41)	1.860(2)		——————
	——————	av.	1.521(13)
av.	1.860(4)		
		av. C—H	1.00(5)
C(7)—C(8)	1.525(3)		

^{a} These bond lengths have not been corrected for thermal motion effects. ^{b} These are average values. The estimated standard deviations have been assigned either from $\sigma_m = \sum\limits_{i=1}^{N} \sigma_i/N$ or from $\sigma_m = \sqrt{\sum\limits_{i=1}^{N} (l_i - \bar{l})/(N-1)}$ depending on which is larger.

An internal check on the precision of this analysis may be made by inspecting cyclohexyl C—C bond lengths, which are assumed to be equal. The average distance is 1.521(13) Å. The error estimate from the observed bond length distribution is about four times larger than the standard deviation derived from the least-squares method. Further inspection of these distances reveals that the bonds on the periphery of the molecule [i.e., those involving C(14), C(24), C(34) and C(44)] show the worst internal agreement. If we omit the eight bonds to these four atoms, the average C—C bond length becomes 1.526(6) Å. We conclude that errors near the center of the molecule have been underestimated by a factor of about two, and that for the molecule as a whole even more caution is required. This conclusion is not surprising, since error estimates from least-squares matrices have often been regarded as optimistic. In addition, atoms near the periphery of a molecule generally have larger thermal motion and are more directly affected by packing forces than are the other atoms.

Results and discussion

As expected, (TME)Ni(TCDP) is found to exist as monomeric molecules in the solid state. The structure confirms that the Ni coordination plane contains

TABLE 4. SELECTED BOND ANGLES (°) IN (TME)Ni(TCDP)

|			
P(1)—Ni—P(2)	91.8(1)	P(1)—C(7)—C(8)	112.4(1)
		P(2)—C(8)—C(7)	112.0(1)
P(1)—Ni—C(3)	112.7(1)		
P(2)—Ni—C(2)	114.8(1)	av.	112.2(3)
av.	113.8(15)[a]	P(1)—C(11)—C(12)	115.8(1)
		P(1)—C(11)—C(16)	111.1(1)
P(1)—Ni—C(2)	152.3(1)	P(1)—C(21)—C(22)	109.8(1)
P(2)—Ni—C(3)	155.1(1)	P(1)—C(21)—C(26)	112.2(1)
		P(2)—C(31)—C(32)	111.2(1)
av.	153.7(20)	P(2)—C(31)—C(36)	115.6(1)
		P(2)—C(41)—C(42)	110.4(1)
C(2)—Ni—C(3)	42.0(1)	P(2)—C(41)—C(46)	111.4(1)
Ni—C(2)—C(3)	69.0(1)	av.	112.2(23)
Ni—C(3)—C(2)	69.0(1)		
		C(16)—C(11)—C(12)	110.7(2)
av.	69.0(1)	C(11)—C(12)—C(13)	111.4(2)
		C(12)—C(13)—C(14)	111.9(2)
Ni—C(2)—C(1)	112.3(2)	C(13)—C(14)—C(15)	111.3(2)
Ni—C(3)—C(6)	110.7(2)	C(14)—C(15)—C(16)	111.4(2)
		C(15)—C(16)—C(11)	110.9(2)
av.	111.5(10)	C(26)—C(21)—C(22)	110.7(2)
		C(21)—C(22)—C(23)	111.4(2)
Ni—C(2)—C(5)	117.0(2)	C(22)—C(23)—C(24)	112.3(2)
Ni—C(3)—C(6)	118.7(2)	C(23)—C(24)—C(25)	110.7(2)
		C(24)—C(25)—C(26)	111.3(2)
av.	117.8(12)	C(25)—C(26)—C(21)	112.8(2)
		C(36)—C(31)—C(32)	110.9(2)
C(1)—C(2)—C(3)	117.2(2)	C(31)—C(32)—C(33)	111.3(2)
C(2)—C(3)—C(6)	118.1(2)	C(32)—C(33)—C(34)	112.2(2)
		C(33)—C(34)—C(35)	111.5(2)
av.	117.6(7)	C(34)—C(35)—C(36)	111.1(2)
		C(35)—C(36)—C(31)	111.8(2)
C(3)—C(2)—C(5)	121.8(2)	C(46)—C(41)—C(42)	110.5(2)
C(2)—C(3)—C(4)	122.5(2)	C(41)—C(42)—C(43)	111.7(2)
		C(42)—C(43)—C(44)	112.4(2)
av.	122.2(5)	C(43)—C(44)—C(45)	110.8(2)
		C(44)—C(45)—C(46)	111.5(2)
Ni—P(1)—C(7)	107.3(1)	C(45)—C(46)—C(41)	112.7(2)
Ni—P(2)—C(8)	107.3(1)		
		av.	111.5(7)
av.	107.3(1)		
Ni—P(1)—C(11)	114.6(1)		
Ni—P(2)—C(31)	117.5(1)		
av.	116.0(21)		
Ni—P(1)—C(21)	125.0(1)		
Ni—P(2)—C(41)	122.7(1)		
av.	123.8(16)		
C(11)—P(1)—C(21)	101.9(1)		
C(11)—P(1)—C(7)	102.4(1)		
C(21)—P(1)—C(7)	102.9(1)		
C(31)—P(2)—C(41)	101.4(1)		
C(31)—P(2)—C(8)	102.2(1)		
C(41)—P(2)—C(8)	103.1(1)		
av.	102.3(6)		

[a] See footnote b of Table 3.
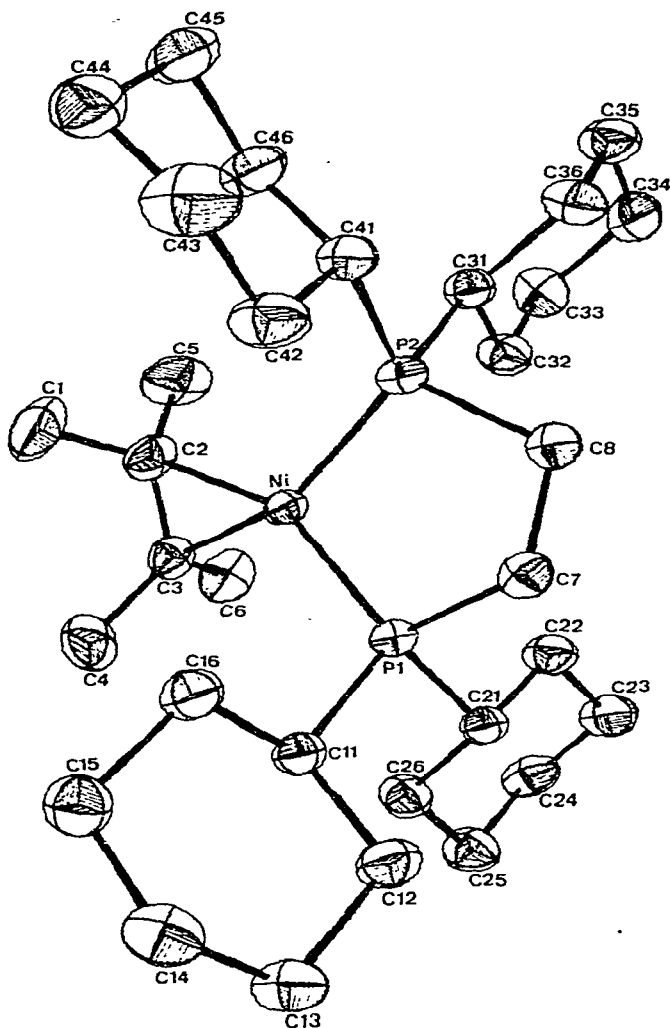
Fig. 1. A perspective drawing of (TME)Ni(TCDP). Hydrogen atoms have been omitted for clarity.

a π-bonded TME moiety and the two phosphorus atoms of the TCDP ligand. Intermolecular non-bonded contacts appear to be normal, the shortest being H(12B)···H(45A) (0.5+x, 0.5−y, z−0.5), 2.28(3) Å.

The chelate phosphine and nickel atom form a heteronuclear five-membered ring. This ring possesses idealized C_2 symmetry. The dihedral angle between the planes Ni,P(1),P(2) and Ni,C(7),C(8) is 18.8°. The torsion angle P(1)—C(7)—C(8)—P(2) (33.7°) is much lower than the *gauche* value. The dihedral angles between the plane of the carbon atoms bonded to a phosphorus atom and the plane of the three cyclohexyl carbon atoms nearest to the phosphorus atom [such as C(11),C(12),C(16)] are a relative measure of the rotation of the cyclohexyl groups about the C—P bonds. These angles are 89.8°, 26.2°, 90.3° and 26.0° for cyclohexyl groups one to four, respectively. Thus the C_2
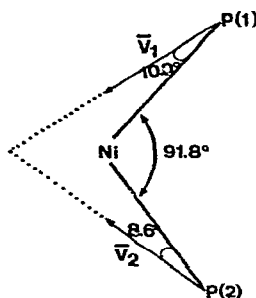
Fig. 2. Orientation of the phosphorus atom three-fold axis ($\bar{V}_1$ and $\bar{V}_2$) with respect to the Ni—P bonds.

symmetry is preserved in the distribution of these angles. The structure of the TCDP ligand contains a number of features which may be compared with those of monophosphine ligands studied recently in this laboratory [9]. The cyclohexyl groups exist in the chair conformation and the phosphorus atoms are bonded equatorially to these fragments. The spread of P—C distances and C—P—C angles are small; the average values for these parameters are 1.860(4) Å and 102.3(6)° respectively. While the C—P—C angles show little variation, the Ni—P—C angles show a wide variation, 107.3(1)—125.0(1)°. This variation results from the structural constraints of the chelate ring and the apparent tendency for the phosphorus atom to possess equal C—P—C angles. Thus the phosphorus three-fold axes $\bar{V}_1$ and $\bar{V}_2$, defined as a line extended from the midpoint of the relevant three bonded carbon atoms through the phosphorus atom P(1) and P(2) respectively, are not colinear with the corresponding Ni—P vectors. The angles $\angle \bar{V}_1$, $\overline{P(1)}$—Ni and $\angle \bar{V}_2$, $\overline{P(2)}$—Ni are 10.0° and 8.6° respectively. The orientation of these vectors are shown in Fig. 2. If one assumes that the phosphorus lone pair is extended along the phosphorus three-fold axis, the Ni—P bonds must be bent.

The P(1)—Ni—P(2) bond angle is 91.8(1)°. For essentially planar, three-coordinate Ni structures, one expects the σ-bond angles at the Ni atom to be approximately 120°. The much smaller P(1)—Ni—P(2) angle observed here undoubtedly is due to the steric constraints of the chelate ligand. Selected structural parameters for a number of $XNiL_2$ compounds (X = π-olefin or σ-nitrogen bonded ligand; L = phosphine or isocyanate ligand) are listed in Table 5.

Since the Ni—P bond length in $(TME)Ni(TCDP)$ and $C_2H_4Ni[P(C_6H_5)_3]_2$ are indistinguishable [2.156(6) Å vs. 2.152(5) Å or 2.16 Å, respectively] despite the 19° difference in the corresponding P(1)—Ni—P(2) angles, we conclude that current structural evidence on $(olefin)Ni(PR_3)_2$ compounds does not indicate that the Ni—P distance is very sensitive either to the P(1)—Ni—P(2) angle or to the alkyl or aryl character of the groups R. On the other hand, the replacement of phenyl groups by the strongly electron withdrawing group o-$OC_6H_4CH_3$ does lead to a significant shortening in the Ni—P length [3d] — compare $C_2H_4Ni[P(C_6H_5)_3]_2$ with $C_2H_4Ni[P(o$-$OC_6H_4CH_3)_3]_2$.

Interestingly, deviations from 120° for L(1)—Ni—L(2) angles of $XNiL_2$ compounds appear to be due to the different steric requirements of the ligands X and L. If we exclude this study, the size of the ligands L listed in Table 5

TABLE 5

GEOMETRIES OF SOME XNiL$_2$ COMPOUNDS

Compound	C=C (Å)	Ni—C (Å)	Ni—P (Å)	L(1)—Ni—L(2) (°)	Ref.
C$_2$H$_4$Ni[P(C$_6$H$_5$)$_3$]$_2$	1.43(1)	1.99(1)	2.152(5)	110.5(2)	25
	1.41	1.94	2.16	111	26
C$_2$H$_4$Ni[P(o-OC$_6$H$_4$CH$_3$)$_3$]$_2$	1.46(2)	2.02(2)	2.095(2)	116.3(2)	3d
(C$_2$H$_3$CN)Ni[P(o-OC$_6$H$_4$CH$_3$)$_3$]$_2$	1.46(2)	2.016(10) (CH$_2$)	2.121(4) (trans-CH$_2$)	110.3(1)	3d
		1.911(12) (CHCN)	2.096(4) (trans-CHCN)		
C$_2$(CN)$_4$Ni[CNC(CH$_3$)$_3$]$_2$	1.476(5)	1.954(4)		98.9(2)	3b
C$_2$(CH$_3$)$_4$Ni[P(C$_6$H$_{11}$)$_2$CH$_2$—]$_2$	1.421(3)	1.981(2)	2.156(6)	91.8(1)	This work
N$_2$ {Ni[P(C$_6$H$_{11}$)$_3$]$_2$ }$_2$			2.18(1)	128(1)	9a

vary as follows: CNC(CH$_3$)$_3$ < P(C$_6$H$_5$)$_3$ < P(o-OC$_6$H$_4$CH$_3$)$_3$ < P(C$_6$H$_{11}$)$_3$ [10]. The ordering of the ligands X according to size would be: N$_2$ ≪ C$_2$H$_4$ < C$_2$H$_3$CN < C$_2$(CN)$_4$. Thus N$_2$[Ni{ P(C$_6$H$_{11}$)$_3$ }$_2$]$_2$ and C$_2$(CN)$_4$Ni[CNC(CH$_3$)$_3$]$_2$ have the largest and smallest L(1)—Ni—L(2) angles respectively. Before an attempt is made to analyze these angles more closely, a more rigorous method for determining the size of X and L should be found.

Apparently the Ni—P bond length increases about 0.04 Å when one PR$_3$ ligand is replaced by ethylene [i.e., the Ni—P distance in (C$_2$H$_4$)$_2$NiP(C$_6$H$_{11}$)$_3$ is 2.196(2) Å [9b]]. It is reasonable to assume that such a replacement would alter the σ acid and π base character of the nickel atom [11].

The TME ligand is considerably distorted from planarity. The major distortion is the bending back of the methyl groups from the nickel atom. The angles α, β$_1$, and β$_2$ may be used to describe such distortions [3b], and their values are 54.5°, 62.3° and 63.2° respectively. The average value of β is 62.8(6)°; therefore the average bending back of the olefin substituents is 90° − β = 27.2(6)°.
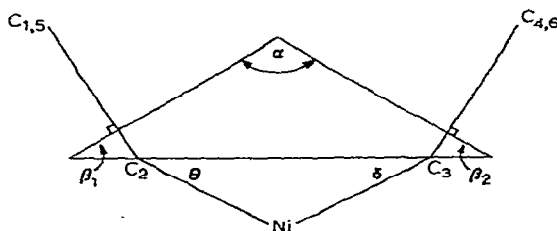
Instead of considering the deformation of the TME ligand from the point of view of a nickelated double bond, one could consider the deformation from the point of view of an idealized heteronuclear three-membered ring. Then we would examine the angle Δβ between a plane normal to the ring and bisecting the endocyclic C—C—Ni angle and the plane of the carbons atoms CMe$_2$, where

Me is a carbon atom of a methyl group [3a]. From the sketch above, $\Delta\beta_1 = \theta/2 - (90° - \beta_1) = 6.8°$ and $\Delta\beta_2 = 7.7°$. Thus the methyl groups are not bent quite as far back from the nickel atom as a heterocyclic three-membered ring model might require. However, non-bonded repulsion between the methyl groups [C(1)···C(4), C(5)···C(6)] would be increased by a further bending back of the CMe_2 planes, and these contacts were found to be short enough, 2.936(3) Å, to indicate that this interaction should not be overlooked. The values of α and β reported for $C_2(CN)_4Ni[CNC(CH_3)_3]_2$ are 56.8(5)° and 61.6(5) respectively, values which are not significantly different from those observed in the TME complex. Although the distortions of these two coordinated olefins are not strictly comparable, since isocyanate ligands and phosphine ligands have different electronic and steric characteristics, clearly an olefin π-bonded to a nickel atom need not be substituted with strong electron withdrawing groups before the metal—olefin interaction is sufficient to cause large distortions in the olefin. Nevertheless, significantly greater amounts of bending back may be introduced by highly electronegative groups; for example, in tetrafluoroethylene-1,1,1-tris(diphenylphosphinomethyl)ethane nickel, the CF_2 groups are bent back by 42° [3f].

A dihedral angle of 16.5° exists between the planes Ni,C(2),C(3) and Ni,P(1),P(2). The relation between the Ni,P(1),P(2) plane and the olefin attachment to the nickel atom is most completely described by the following quantities: *(1)* the distance from the midpoint of the C(2)—C(3) bond to the Ni,P(1), P(2) plane is 0.046(3) Å, *(2)* the angle of 73.5° between the C(2)—C(3) vector and the normal to the Ni,P(1),P(2) plane. Thus the symmetry of the molecule is approximately C_2, which is the same as that of the TCDP ligand. That an olefin bonded to a zero valent transition metal is twisted out of a natural coordination plane of the metal atom is frequently reported. The problem has received theoretical attention, but the results of these studies are conflicting.

Molecular orbital calculations on platinum compounds indicate no twist [12]. Theories based either on a spontaneous torsion about the olefin double bond [13] or on a back-bond donation induced Jahn—Teller effect [14] predict that a small twist might lead to a structure of low energy. In this connection it must be recalled that in the crystal structure of optically active fumaric acid irontetracarbonyl, twist angles of 17°, 17° and 0° are reported for the three independent molecules in the asymmetric unit. Thus small twist angles may also reflect a minimization of crystal energy [15].

The observation that the corresponding complex with two $P(C_6H_{11})_3$ ligands could not be prepared [2] indicates that the steric interactions between the phosphine and olefin ligands can be important in determining the stability and perhaps also the geometry of the complexes. The olefin twist angle in an isolated molecule should reflect a minimization of the total energy (steric and electronic) of the molecule. In this case the relevant steric interactions are those between the potential energy surfaces of the TME and TCDP ligands. Only seven intramolecular apparent H(TME)···H(TCDP) contacts are less than 2.9 Å (Fig. 3). If one considers those contacts less than 2.6 Å to be repulsive in nature, each of these five interactions would tend to increase the twist angle (Fig. 3). Only one intermolecular H···H(TME) distance, H(45B) ($-x,1-y, -z$)···H(1B), of 2.37(4) Å is less than 2.6 Å, and this contact would tend to decrease the
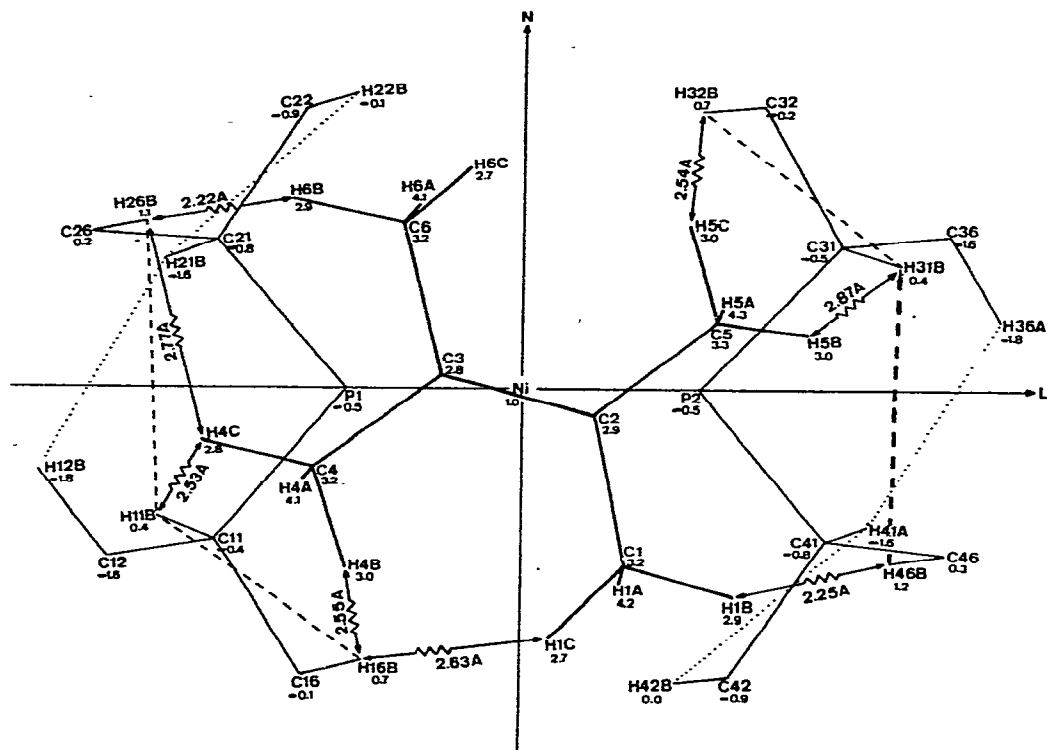
Fig. 3. Intramolecular H(TME)···H(TCDP) non-bonded contacts as seen looking along the approximate molecular two-fold axis. The dotted and dashed lines delineate regions of weaker and stronger repulsion, respectively. The number next to the atom labels give the depth of the atom in projection.

twist angle. The asymmetry of the intramolecular repulsions with respect to the Ni,P(1),P(2) plane result from the unequal amounts of rotation of the cyclohexyl groups about the C—P bonds mentioned previously. Unfortunately the large size of this molecule and our ignorance of so many of the required potential functions prohibits a rigorous examination of the non-bonded interactions. At this point, however, an electronic explanation for the observed non-zero twist angle would not appear to be necessary.

The torsion angles C(1)—C(2)—C(3)—C(4) and C(5)—C(2)—C(3)—C(6) are 6.4° and 6.6° respectively. Recent force-field calculations on TME predict a 4.3° torsion about the double bond [16]. Noting that the absolute values of the torsion angles Ni—C(2)—C(3)—Me or Me—C(2)—C(3)—Ni are smallest for those methyl carbons most removed from the plane Ni,P(1),P(2) (Table 6), one can conclude that the torsions about the C(2)—C(3) bonds rotate the p-π orbitals of the carbon atoms slightly toward the Ni,P(1),P(2) plane. Similar distortions do not always appear in olefin complexes. In $C_2(CN)_4Ni[CNC(CH_3)_3]_2$, the cyanide groups are within 3.0° of being eclipsed, but the sense of these slight rotations are not those required to point both olefin p-π orbitals towards the NiC_2(isocyanide) plane. Apparently the significance of these small torsion angles should not be overemphasized.

An examination of the thermal elipsoids of the TME carbon atoms displayed in Fig. 1 indicated that the thermal motion of the (TME)Ni fragment

TABLE 6

SELECTED NICKEL—OLEFIN TORSION ANGLES IN (TME)Ni(TCDP)

Atoms	Torsion angles (°)	Deviation (Å) from Ni,P(1),P(2) plane	
Ni—C(2)—C(3)—C(4)	111.4	C(4)	0.759
Ni—C(3)—C(2)—C(5)	109.6	C(5)	—0.673
C(1)—C(2)—C(3)—Ni	—105.0	C(1)	1.728
Ni—C(2)—C(3)—C(6)	—103.0	C(6)	—1.598

might well be described by a rigid-body motion approximation. Therefore the 54 thermal motion parameters of atoms Ni,C(1)···C(6) were fit by the method of least-squares to the 20 parameters of the translational T, librational L and screw correlational S tensors of Schomaker and Trueblood's [17] rigid-body motion model. These three tensors, defined in a Cartesian coordinate system with axes parallel to the crystal a, b, c^*, were then transformed to the special axis system of the molecular fragment in order to expedite further analysis. The special axis system has $x = \overline{\text{Ni—M}}$ (M is the midpoint of TME double bond), $y =$ vector normal to Ni,C(2),C(3) plane and $z = x \times y$ [approximately parallel to $\overline{C(2)—C(3)}$]. The translational motion is nearly isotropic as can be seen by the r.m.s. aplitudes along the principal axes of T: 0.22, 0.22 and 0.20 Å. The librational motion is definitely anisotropic, the major axis of libration being approximately parallel to $\bar{x}$. The r.m.s. difference of the observed and calculated $U(I,J)$'s is 0.0027 Å. Since the r.m.s. $\Delta[U(I,J)]$ is 0.0014 Å, some non-rigid-body motion may be present; therefore, the amounts of rigid-body motion could be overestimated.

Conceivably, the large libration about the $\overline{\text{Ni—M}}$ vector could be due to an oscillation of the olefin about this vector, which would be a non-rigid-body motion feature for the molecule as a whole. Accordingly, the T, L and S tensors were calculated from the $U(I,J)$'s of the Ni(TCDP) fragment of the molecule. Not surprisingly, the r.m.s. difference of the observed and calculated $U(I,J)$'s is higher, 0.0077 Å. Then the rigid-body motion of the Ni(TCDP) fragment was subtracted from the thermal motion tensors of the non-hydrogen atoms of the (TME)Ni part. With these new parameters the T, L and S tensors were recalculated and transformed to the special axial system. Of the twenty unique elements of these three tensors, only $L(1,1)$ and $L(3,3)$, 0.0158(10) and 0.0072(10) rad^2 respectively, were found to be significantly non-zero. The largest of these, $L(1,1)$, corresponds to the mean square libration of the olefin about the X vector. We approximate the rotational barrier of the TME about X by the two-fold cosine potential function $V = 0.5V_0(1 - \cos 2\phi)$, where V_0 is the barrier height and ϕ is the rotation coordinate. From the harmonic oscillator approximation to the restricted rotor:

$$\langle \phi^2 \rangle = \frac{h \coth}{8\pi^2} \frac{h\nu/2kT}{I\nu} \quad \text{and} \quad \nu = \frac{1}{\pi} \sqrt{\frac{V_0}{2I}}$$

where I is the moment of inertia and T is the temperature in degrees Kelvin. By equating $L(1,1)$ to $\langle \phi^2 \rangle$, we find that $V_0 = 18$ Kcal/mole. The precision of this number is $\approx 10\%$, but the error in the barrier height may be larger due to sys-

tematic errors in the X-ray thermal parameters and to the approximations involved in the analysis.

Since this barrier height has been determined in the crystal, no meaningful comparison can be made with those barriers determined in solution or those resulting from theoretical calculations, unless the intermolecular contribution to the potential can be shown to be negligibly small with respect to the intramolecular potential, at least near the bottom of the potential well. Recalling that the shortest H(TME)···H(TCDP) contacts are intramolecular rather than intermolecular and assuming that the electroneutrality principle is followed by this molecule, we may make some meaningful comparisons. Clearly the observed barrier is not much larger than those reported for Pt^{II}—olefin compounds in solution, 10—15 kcal/mole [18]. This result is surprising in that a barrier to rotation in $C_2H_4Pt(PH_3)_2$ has been calculated to be 76 kcal/mole [12]. On the other hand, a barrier height of 10(2) kcal/mole has been reported for $(C_2H_4)_2NiP(C_6H_{11})_3$ [19]. If, as claimed by others [12,18], these barriers increase as the amount of metal—olefin π-bonding increases, the amount of π-bonding in Ni^0—olefin compounds is about the same as in Pt^{II}—olefin compounds. The low value for the barrier is also an interesting commentary on the twist angles (vide supra) observed in a number of metal—olefin structures.

The C—C and Ni—C bond lengths of the nickel—TME fragment were corrected for the effects of librational shortening [17]. The average C—Me bond distance is 1.517(15) Å (corrected, 1.534 Å). The C—C—Me bond angles fall into two groups; two angles averaging 122.2(5)° and two smaller angles averaging 117.6(7)°. All four angles can no longer be equal due to the previously-mentioned twisting about the central bond of this non-planar species. The average value of all four angles is 119.9°. The angles are all somewhat smaller than the corresponding ones measured on TME by the electron diffraction technique [124.2(20)°] [20], which is in good agreement with the results of thermochemical force field calculations, 124.8° [21]. The decrease in these angles results from the bending back of the olefin substituents while the Me—C—Me bond angles are kept constant; compare our average Me—C—Me angle 111.8(9)° with the 111.5(20)° angle from electron diffraction or the 110.4° angle from calculation for TME.

Neither the C=C distance [1.421(3) Å, corrected 1.433 Å)] nor the average Ni—C bond length [1.981(2) Å, corrected 1.993 Å] differs significantly from the corresponding bond lengths in the other monoethylene complexes of nickel(0) listed in Table 5. In each case the coordinated olefin central bond length is significantly longer (0.07—0.14 Å) than in the free hydrocarbons, 1.34 Å. Shorter Ni—C bond distances result when one or more CN groups are bonded to the olefin (i.e. 1.911(12) Å in $(C_2H_3CN)Ni[P(o-OC_6H_4CH_3)_3]_2$ [3d] and 1.954(4) Å in $C_2(CN)_4Ni[CNC(CH_3)_3]_2$ [3b]). In addition, the C=C distance observed in this study is shorter than that in the tetracyanoethylene complex, 1.476(5) Å [3b].

If a stronger Ni—olefin interaction is indicated by a lengthening of the C=C bond length and a shortening of the Ni—C bond length, present bond length data appears to be in conflict with the observation [2] that the Ni—ethylene interaction is stronger than the Ni—TME interaction. Perhaps the use of different phosphine ligands as well as experimental errors in the determinations have

obscured any small trends. On the other hand, bond length data does indicate that cyano-group substituted olefins interact more strongly with Ni^0 than TME or ethylene [3b]. Indeed $C_2(CN)_4Ni(TCDP)$ is reported to be very stable with respect to replacement of tetracyanoethylene by ethylene [2].

The commonly accepted theory of metal—olefin bonding is the σ, π-scheme of Dewar and Chatt [22,23]. The olefin donates its π-electrons to the metal atom to form a σ-bond, and the metal donates two d electrons to the olefin π^* orbital to form a π-bond. When both the σ- and π-bonds are necessary to describe the bonding, two electrons are present for each metal—carbon bond. The $Ni—C(sp^3)$ bond length in various Ni^{II} complexes is about 1.95 Å [9f]. Thus the $Ni—C$(olefin) bond lengths observed to date (Table 5) seem to be short enough to imply important σ- and π-bonding. The suggested nickelo-cyclopropane structure should not be seen as implying sp^3 hybridizing ring carbon atoms. Some calculations on cyclopropane for example, indicate that the C—C bond orbitals have higher carbon atom p character, $sp^{\approx 4.5}$, than do orbitals involved in the C—H bonds, $sp^{\approx 2.1}$ [24]. The distortions of the olefin (increase of the C=C bond length, nonplanarity of the olefin) brought about by coordination are credited to the electron density in the olefin π^* orbitals. In addition, the π-bond is believed to be responsible for the electronic component of the barrier to olefin rotation. This theory predicts that the presence of electronegative groups such as CN on the olefin increase the strength of the metal—olefin π-bond while the σ-bond is weakened [3c], a prediction which is consistent with bond length and chemical evidence (vide supra). However, no quantitative relationship between the observed amounts of bending back of the olefin substituents from the metal atom and the corresponding length of the coordinated C=C bond is observed. Whether this indicates that mixing of olefin $2s$ and $2p$ orbitals, nonbonded repulsions and consideration of excited states of the metal and olefin are necessary additions to the theory of the metal—olefin interaction remains to be answered.

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