

## Di- $\mu$ -hydrido-bis[1,3-propanebis(dicyclohexylphosphine)]dinickel-(Ni–Ni) – The Bonding in a Three-center Hydrogen-bridged Ni–Ni System

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The crystal structure of the title compound,  $[(C_6H_{11})_2PCH_2CH_2CH_2P(C_6H_{11})_2NiH]_2$  (1), has been determined from 4051 reflections and refined to a final  $R$ -value of 0.044. The positions of the hydrogen atoms (bridging and non-bridging) have been determined from a difference Fourier synthesis. The molecular structure of the diamagnetic compound consists of subunits doubly-bridged by hydrogen atoms. The Ni–Ni and average Ni–H distances are 2.441 and 1.6 Å, respectively. In the solid state the two planes of the  $P_2Ni$  units form a dihedral angle of 63.3°. Theoretical considerations predict a square-planar structure for the idealized molecule with a soft potential energy surface for a twisting motion towards the observed geometry. The observed twist is the result of severe intramolecular repulsions between the cyclohexyl groups of the two  $P_2Ni$  units.

Di- $\mu$ -hydrido-bis[1,3-propanebis(dicyclohexylphosphin)]dinickel(Ni–Ni) – Der Bindungszustand in einem Dreizentren-Wasserstoff-überbrückten Ni–Ni-System

Die Kristallstruktur der Titelverbindung  $[(C_6H_{11})_2PCH_2CH_2CH_2P(C_6H_{11})_2NiH]_2$  (1) wurde aus 4051 Reflexen abgeleitet und zu einem  $R$ -Wert von 0.044 verfeinert. Lageparameter aller Wasserstoffatome konnten einer Differenz-Fourier-Synthese entnommen werden. Die Struktur der diamagnetischen Verbindung setzt sich aus zwei  $P_2Ni$ -Untereinheiten zusammen, welche zweifach mit Wasserstoffatomen (Ni–H 1.6 Å) überbrückt sind. Hierdurch ergibt sich ein bindender Ni–Ni-Abstand von 2.441(1) Å. Im Kristallgitter bilden die Ebenen durch die  $P_2Ni$ -Untereinheiten einen Interplanarwinkel von 63.3°. Theoretische Betrachtungen sagen für das freie Molekül eine quadratisch planare Anordnung voraus, doch ergibt sich für die Drehbewegung zur beobachteten Geometrie nur eine flache Potentialenergiefläche. Die gefundene Verdrillung resultiert aus starken intramolekularen Abstoßungskräften zwischen den Cyclohexylgruppen der zwei  $P_2Ni$ -Einheiten.

### Introduction

Polynuclear metal hydride complexes, in which hydrogen atoms bridge two or more transition metals, are well known<sup>1)</sup>.

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Structural investigations on M-H-M systems have been reported for the compounds  $\text{HMn}_2(\text{PPh}_2)(\text{CO})_8^{2)}$  and  $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{H}[\text{P}(\text{CH}_3)_2](\text{CO})_4^{3)}$  among others<sup>4)</sup>. In  $\text{HCr}_2(\text{CO})_{10}^-$  a linear three-center one electron pair bond has been established<sup>5)</sup>. We undertook a structural determination of the hydrogen-bridged Ni-Ni system,  $[(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_{11})_2\text{NiH}]_2$  (**1**)<sup>6)</sup>, because NMR investigations of this and related compounds indicated that the heavy atom skeleton may be planar.

## Experimental

Crystals of the title compound **1** were crystallized from toluene/ether as dark red plates. A crystal of the approximate dimensions  $0.12 \times 0.35 \times 0.44$  mm was sealed under dry argon in a thin-walled glass capillary and was used for all subsequent measurements. Weissenberg and precession photographs indicated triclinic symmetry of the reciprocal lattice. Accurate dimensions (see Table 1) of the unit cell were determined from a least-squares treatment of the angular settings for 40 high angle reflections, determined with a computer operated 4-circle Siemens-Hoppe-diffractometer, using  $\text{Cu K}\alpha$  radiation.

Table 1. Crystal Data of **1**

$[(\text{C}_6\text{H}_{11})_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_{11})_2\text{NiH}]_2$ , MW = 992.52	
$a = 12.040(6)$ Å	$V = 2789.8$ Å <sup>3</sup>
$b = 24.20(1)$ Å	$\lambda = 1.54178$ Å (Cu $K\alpha$ )
$c = 11.75(2)$ Å	space group $P\bar{1}$
$\alpha = 103.92(6)^\circ$	$d_{\text{calc}} = 1.180$ gcm <sup>-3</sup>
$\beta = 117.82(6)^\circ$	$Z = 2$
$\gamma = 99.04(5)^\circ$	$\mu = 20.89$ cm <sup>-1</sup> (Cu $K\alpha$ )

The calculated density, assuming 2 molecules of **1** per unit cell, is 1.180 gcm<sup>-3</sup>. The experimental density could not be measured, due to the instability of the compound.

The intensities of 5713 independent reflections were measured using the 5-step  $\Theta/2\Theta$  scan procedure<sup>7)</sup>, with Ni filtered  $\text{Cu K}\alpha$  radiation, within the sphere  $2\Theta \leq 104^\circ$ . The crystal, which gave satisfactory  $\Omega$  scans in all directions was aligned with the  $\Phi$  axis of the diffractometer coincident with the [100] axis of the cell. Only one reference reflection (0 4 -2) could be monitored every twenty reflections due to limitations of the diffractometer software. The intensity of this monitored reflection decreased during the data collection period by 15%. This decrease was corrected for by a rescaling procedure during the subsequent data reduction process, in which the data set was also corrected for Lorentz and polarization effects. 4051 observed reflections with  $I > 2\sigma(I)$  were

<sup>2)</sup> R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Am. Chem. Soc.* **89**, 4323 (1967).

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<sup>4)</sup> M. R. Churchill, S. W.-Y. Ni Chang, M. L. Berch, and A. Davidson, *J. Chem. Soc., Chem. Commun.* **1973**, 691; M. R. Churchill and S. W.-Y. Ni, *J. Am. Chem. Soc.* **95**, 2150 (1973); S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.* **95**, 4532 (1973); M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J. Chem. Soc., Chem. Commun.* **1976**, 671.

<sup>5)</sup> L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Am. Chem. Soc.* **88**, 366 (1966); L. B. Handy, J. K. Ruff, and L. F. Dahl, *ibid.* **92**, 7312 (1970).

<sup>6)</sup> K. Jonas and G. Wilke, *Angew. Chem.* **82**, 295 (1970); *Angew. Chem., Int. Ed. Engl.* **9**, 312 (1970).

<sup>7)</sup> C. Krieger, *J. Organomet. Chem.* **22**, 697 (1970); *Angew. Chem.* **84**, 412 (1972); *Angew. Chem., Int. Ed. Engl.* **11**, 387 (1972).

assigned weights based on counting statistics  $w^{-1} = \sigma^2(\text{counter}) + (0.03 I)^2$  and used in the solution and refinement of the structure. As there was no systematic variation of intensity with  $\Phi$  for the (100)-reflection at  $X 90^\circ$  and  $\mu = 20.89 \text{ cm}^{-1}$ , the data set was not corrected for absorption.

## Solution and Refinement

The coordinates of 2 Ni atoms and 4 P atoms were taken from a sharpened three dimensional Patterson map. A structure factor calculation, including these 6 atoms, yielded a conventional  $R$  value of 0.395 (defined as  $R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$ ). In a subsequent Fourier map, all 54 carbon atoms of the molecule could be clearly identified. Five cycles of full matrix least-squares refinement of positional and isotropic thermal parameters of these 60 atoms gave an  $R$  value of 0.15. An additional 5 cycles of block diagonal least-squares refinement ( $18 \times 18$  blocks) of positional and anisotropic thermal parameters converged at  $R = 0.0747$ . At this point, 12 hydrogen atoms of the  $C_3$  groups at the phosphorus atoms as well as the 2 bridging hydrogen atoms were clearly evident from a difference Fourier map. The remaining positions for the hydrogen atoms on the cyclohexyl rings were computed from the carbon positions and agreed all with positions of positive electron density in the difference map. A final 5 cycles of block diagonal least squares refinement, including all hydrogens with isotropic thermal parameters, gave an  $R$  value of 0.0445 and  $R_w$  of 0.035. A difference map at this stage indicated no electron density greater than  $0.3 \text{ e}/\text{\AA}^3$ . In the refinement, the quantity minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1.0/\sigma^2 |F_o|$ . Atomic scattering factors used were those of *Cromer and Waber*<sup>8)</sup> for non-hydrogen atoms, and those of *Stewart, Davidson, and Simpson*<sup>9)</sup> for hydrogen. The real part of the anomalous dispersion for nickel and phosphorus was corrected for with values given by *Cromer and Liberman*<sup>10)</sup>. The final atomic coordinates are listed in Table 2. The table of the final  $F_o$  and  $F_c$  values for the reflections used in the final refinement cycle and the table of the atomic thermal parameters are available as supplementary material.

## Description of the Molecular Structure

The molecule of **1**, as shown in Fig. 1, consists of two  $P_2Ni$  units, connected through two hydrogen bridges and a Ni–Ni bond of 2.441(1) Å. The two PNiP planes form a dihedral angle of  $63.3^\circ$ . The central  $Ni_2H_2$  plane bisects this dihedral angle.

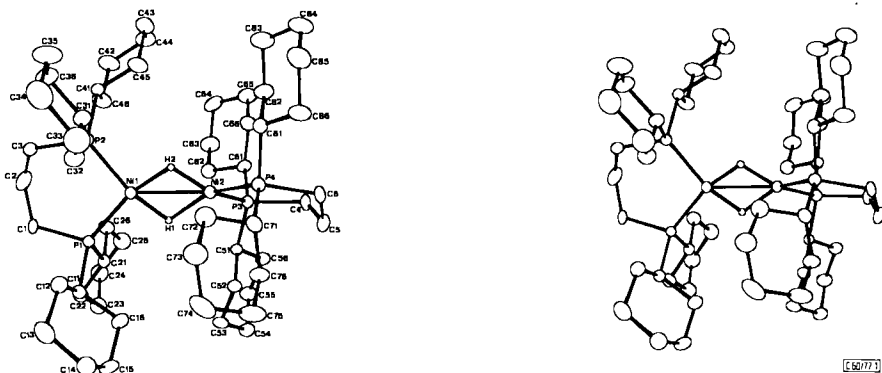


Fig. 1. Stereoscopic view of the thermal ellipsoids of the title compound **1**, scaled to a 20% probability level

<sup>8)</sup> D. T. Cromer and J. T. Waber, *Acta Crystallogr.* **18**, 104 (1965).

<sup>9)</sup> R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.* **42**, 3175 (1965).

<sup>10)</sup> D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53**, 1891 (1970).

Table 2. Final atomic coordinates and their standard deviations ( $\times 1000$ )

ATOM	X	Y	Z	ATOM	X	Y	Z	ATOM	X	Y	Z
Ni1	4460(1)	2450(1)	7081(1)	ATM	C83	8739(5)	4480(2)	2818(6)	Ni5B	2191(4)	4286(18)
Ni2	3201(1)	2166(1)	1805(1)	C84	10256(6)	4606(2)	3297(16)	H46A	5511(38)	2191(4)	1174(42)
P1	4737(1)	3181(1)	3777(1)	C85	10039(5)	3577(2)	2963(16)	H46B	5695(33)	5511(38)	2191(4)
P2	4311(1)	2130(1)	1448(1)	H1A	1428(46)	1692(20)	2550(46)	H47A	4220(36)	4220(36)	5668(34)
P4	7693(1)	2615(1)	1350(1)	H1B	2886(46)	3422(20)	3356(47)	H57A	4482(35)	1237(16)	-5668(37)
C1	7278(1)	3278(1)	1883(1)	H3A	3603(34)	4477(15)	4357(35)	H57B	2894(34)	4220(36)	-2270(36)
C2	3566(1)	3594(1)	3704(1)	H3B	3704(37)	2077(16)	4107(38)	H58A	2671(38)	154(15)	-4220(36)
C3	5612(6)	2071(2)	2155(4)	H4B	6070(37)	1875(38)	3107(38)	H58B	2671(38)	184(15)	-2270(36)
C4	6748(5)	2277(2)	-1493(4)	H6A	8811(37)	2285(16)	2253(38)	H59A	1174(35)	-145(16)	-4458(36)
C5	8931(4)	2798(2)	770(4)	H6B	8120(39)	4872(15)	3737(39)	H59B	1059(35)	878(17)	-4673(39)
C6	4451(1)	2798(2)	3781(4)	H7A	1820(34)	2882(15)	2938(34)	H59C	1059(35)	183(16)	-5713(38)
C7	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H60A	2058(32)	1720(14)	-4591(33)
C8	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H60B	2058(32)	1720(14)	-4591(33)
C9	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H61A	2430(34)	1664(14)	-2781(34)
C10	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H61B	2430(34)	1664(14)	-2781(34)
C11	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H62A	1648(36)	2274(16)	-2781(34)
C12	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H62B	1648(36)	2274(16)	-2781(34)
C13	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H63A	2065(38)	4176(16)	-2781(34)
C14	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H63B	2065(38)	4176(16)	-2781(34)
C15	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H64A	7659(45)	3070(19)	-3014(46)
C16	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H64B	7659(45)	3070(19)	-3014(46)
C17	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H65A	1517(43)	3045(19)	-3781(44)
C18	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H65B	4235(40)	4382(17)	-3781(44)
C19	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H66A	4235(40)	4382(17)	-3781(44)
C20	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H66B	4235(40)	4382(17)	-3781(44)
C21	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H67A	5298(34)	3515(16)	-1761(34)
C22	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H67B	5298(34)	3515(16)	-1761(34)
C23	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H68A	3459(31)	2763(13)	-2951(31)
C24	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H68B	3459(31)	2763(13)	-2951(31)
C25	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H69A	8779(33)	2668(13)	-3741(32)
C26	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H69B	8779(33)	2668(13)	-3741(32)
C27	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H70A	8951(41)	1922(16)	5033(42)
C28	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H70B	8951(41)	1922(16)	5033(42)
C29	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H71A	8620(38)	917(17)	4570(41)
C30	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H71B	8620(38)	917(17)	4570(41)
C31	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H72A	7249(39)	1124(17)	2332(40)
C32	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H72B	7249(39)	1124(17)	2332(40)
C33	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H73A	8066(33)	561(17)	1374(40)
C34	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H73B	8066(33)	561(17)	1374(40)
C35	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H74A	6638(37)	4426(15)	1061(38)
C36	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H74B	6638(37)	4426(15)	1061(38)
C37	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H75A	7848(33)	4455(17)	516(40)
C38	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H75B	7848(33)	4455(17)	516(40)
C39	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H76A	8271(33)	272(17)	2591(33)
C40	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H76B	8271(33)	272(17)	2591(33)
C41	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H77A	7916(33)	3768(15)	1039(36)
C42	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H77B	7916(33)	3768(15)	1039(36)
C43	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H78A	1076(44)	4544(18)	3681(42)
C44	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H78B	1076(44)	4544(18)	3681(42)
C45	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H79A	1704(42)	5039(18)	3896(43)
C46	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H79B	1704(42)	5039(18)	3896(43)
C47	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H80A	8271(33)	4875(18)	7411(42)
C48	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H80B	8271(33)	4875(18)	7411(42)
C49	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H81A	11840(42)	4278(19)	4781(42)
C50	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H81B	11840(42)	4278(19)	4781(42)
C51	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H82A	11840(42)	4278(19)	4781(42)
C52	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H82B	11840(42)	4278(19)	4781(42)
C53	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H83A	11840(42)	4278(19)	4781(42)
C54	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H83B	11840(42)	4278(19)	4781(42)
C55	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H84A	1074(42)	5140(43)	4371(48)
C56	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H84B	1074(42)	5140(43)	4371(48)
C57	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H85A	11840(42)	3327(16)	3371(48)
C58	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H85B	11840(42)	3327(16)	3371(48)
C59	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H86A	10189(43)	2151(44)	2151(44)
C60	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H86B	10189(43)	2151(44)	2151(44)
C61	5073(5)	297(2)	3240(5)	H8B	7186(38)	2009(17)	-1513(35)	H87A	4134(43)	4134(43)	571(37)
C62	4909(5)	367(2)	1798(5)	H7A	4420(33)	1846(14)	4399(34)	H87B	4134(43)	4134(43)	571(37)
C63	4351(1)	1251(2)	3781(4)	H7B	1820(34)	2882(15)	2938(34)	H88A	5594(40)	2813(18)	2023(41)
C64	4757(5)	707(2)	4163(5)	H8A	1185(65)	2854(32)	2673(67)	H88B	5594(40)	2813(18)	2023(41)

[C60] 774z

The two hydrogen atoms are within the limits of the experimental error equidistant to both Ni atoms as observed in other three-center M–H–M systems<sup>3)</sup>. The averaged nickel hydrogen distances of 1.6 Å correspond to the sum of the covalent radii<sup>11)</sup> and correspond to the distance postulated in the crystal structure analysis of a non-stoichiometric hydrido complex of nickel with the tetradentate ligand N(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub><sup>12)</sup>. The presence of a quartet for the hydridic hydrogen atoms in the NMR spectrum of **1**<sup>6)</sup> suggested a tetrahedral arrangement around the nickel, however, simulation of the spectrum has shown that the observed spectrum is consistent with the distorted square-planar arrangement found in the solid state<sup>13)</sup>. An idealized square-planar arrangement in which all the nickel and phosphorus atoms lie in a common plane would cause severe overlap between ring 2 (C<sub>21</sub>–C<sub>26</sub>) and 6 (C<sub>61</sub>–C<sub>66</sub>); ring 3 and 7; and ring 4 and 8, with H–H contacts less than 1.8 Å. In the observed distorted conformation, the observed distances between these hydrogen atoms are 5.5 Å.

The bidentate bis(phosphino)propane and the nickel atoms form heteronuclear six-membered rings in the chair conformation with idealized symmetry *m*<sup>14)</sup>. All four Ni–P distances (average 2.134(3) Å) are slightly shorter than those usually found in related Ni-phosphine complexes<sup>15)</sup>. The coordination of the phosphorus atoms is that of a distorted tetrahedron. The Ni–P–C(cyclohexyl) angles may be divided into two groups: those in which the P–C(cyclohexyl) bonds are equatorial to the Ni–H group and close to the Ni<sub>2</sub>H<sub>2</sub> plane have an average value of 119.1(8)°; those axial to the coordination plane are significantly smaller (113.3(4)°). As a result these cyclohexyl groups bend towards the Ni–Ni system. The range of P–C distances, including those to the C<sub>3</sub> fragments of

Table 3. Bond distances in Å

Ni1–H1	1.62 (4)	C1–C2	1.500(9)	C43–C44	1.531(10)	C72–C73	1.539(9)
Ni1–H2	1.54 (4)	C2–C3	1.419(10)	C44–C45	1.513(10)	C73–C74	1.509(9)
Ni2–H1	1.68 (4)	C4–C5	1.531(8)	C45–C46	1.530(8)	C74–C75	1.511(10)
Ni2–H2	1.49 (5)	C5–C6	1.523(9)	C46–C47	1.519(9)	C75–C76	1.537(8)
Ni1–Ni2	2.443(1)	C11–C12	1.518(9)	C51–C52	1.523(7)	C76–C77	1.511(9)
Ni1–P1	2.129(2)	C12–C13	1.547(8)	C52–C53	1.529(8)	C81–C82	1.513(8)
Ni1–P2	2.136(2)	C13–C14	1.506(10)	C53–C54	1.531(9)	C82–C83	1.518(9)
Ni2–P3	2.134(2)	C14–C15	1.510(10)	C54–C55	1.519(8)	C83–C84	1.526(11)
Ni2–P4	2.135(2)	C15–C16	1.535(8)	C55–C56	1.513(8)	C84–C85	1.521(9)
P1–C1	1.864(2)	C16–C17	1.523(9)	C56–C57	1.538(8)	C85–C86	1.514(9)
P1–C11	1.850(5)	C21–C22	1.518(8)	C61–C62	1.520(8)	C86–C87	1.546(9)
P1–C21	1.882(6)	C22–C23	1.545(9)	C62–C63	1.529(9)	C31–C32	1.521(8)
P2–C3	1.833(7)	C23–C24	1.518(9)	C63–C64	1.498(9)	C32–C33	1.507(10)
P2–C31	1.877(6)	C24–C25	1.520(9)	C64–C65	1.517(11)	C33–C34	1.518(10)
P2–C41	1.848(6)	C25–C26	1.526(8)	C65–C66	1.513(8)	C34–C35	1.485(10)
P3–C4	1.855(6)	C26–C27	1.534(8)	C66–C67	1.503(8)	C35–C36	1.537(10)
P3–C51	1.850(5)	C31–C32	1.517(8)	C71–C72	1.517(9)	C36–C37	1.524(9)
P3–C61	1.864(5)	C32–C33	1.535(8)				
P4–C6	1.875(6)						
P4–C71	1.857(6)						
P4–C81	1.828(6)						

[C 60/77 Tab. 3]

<sup>11)</sup> G. R. Davies, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A* **1967**, 1750; C. Krüger, unpublished results.

<sup>12)</sup> L. Sacconi, A. Orlandini, and S. Midollini, *Inorg. Chem.* **13**, 2850 (1974).

<sup>13)</sup> J. Brandt, Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, private communication.

<sup>14)</sup> The Ni–P–C angles of these rings (116.5° (1.0)) indicate a loss of strain as compared to the corresponding angles in five-membered chelate systems (107.3°).

<sup>15)</sup> D. J. Brauer and C. Krüger, *J. Organomet. Chem.* **77**, 423 (1974), and literature cited therein.

Table 4. Bond angles in degrees

H1–Ni1–P1	87.3(1.5)	H2–Ni1–P2	90.9(1.8)
H1–H11–H2	81.5(2.4)	P1–Ni1–P2	103.5(1)
H1–Ni2–P3	93.0(1.5)	H2–Ni2–P4	101.3(1.8)
H1–H12–H2	78.9(2.3)	P3–Ni2–P4	102.7(1)
C21–P3–Ni1	113.9(2)	C11–P1–Ni1	121.0(2)
C31–P2–Ni1	113.9(2)	C41–P2–Ni1	118.8(2)
C51–P3–Ni2	112.9(2)	C61–P3–Ni2	119.8(2)
C81–P4–Ni2	113.2(2)	C71–P4–Ni2	116.7(2)
C1–P1–Ni1	116.2(2)	P1–C1–C2	116.8(4)
C3–P2–Ni1	116.7(2)	P2–C3–C2	116.5(5)
C5–P3–Ni2	115.4(2)	P3–C4–C5	114.5(4)
C8–P4–Ni2	117.8(2)	P4–C6–C5	114.5(4)
C1–C2–C3	126.7(6)	C4–C5–C6	114.2(5)

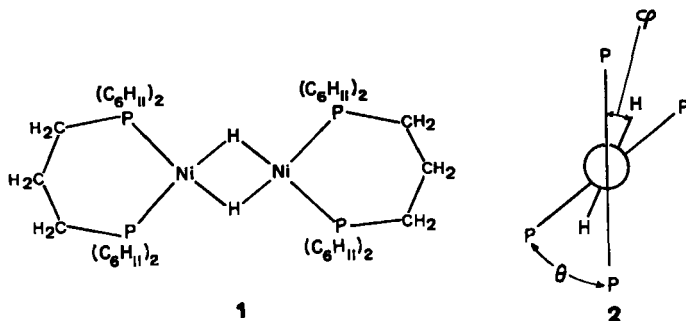
[CSD777 tab.4]

the chelating system, is small. Carbon atom C2 shows slight disorder, as indicated by its thermal parameters and its unusual bond lengths to the neighbouring atoms.

All cyclohexyl groups are in the chair conformation and bonded equatorially to the phosphorus atoms. Important bond angles and distances are given in Tables 3 and 4 and Figs. 2 and 3. Intermolecular contacts less than 3.8 Å are observed only between cyclohexyl rings of adjacent molecules. The shortest C–C distance is C63–C73' (3.66 Å).

## Discussion

As indicated above, the structure of the  $P_2NiH_2NiP_2$  dimer **1** may be described as a distorted square-planar dimer in which the  $PNiP$  planes are twisted away from one another so that the  $P_2NiH_2NiP_2$  moiety adopts an approximate  $D_2$  symmetry.



We have calculated a potential energy surface for a model<sup>16)</sup>  $P_4Ni_2H_2$  molecule containing an idealized  $NiH_2Ni$  rhombus. Two torsional degrees of freedom have been defined as follows: looking down the Ni–Ni axis, with one P–Ni–P unit frozen, the other P–Ni–P plane was rotated by an angle  $\Theta$ , and the H–H line by angle  $\phi$ . This is illustrated in 2.

The observed solid state structure has  $\Theta = 63.3^\circ$  and the hydrogens (slightly moved by our idealization) near  $\phi = 30^\circ$ .

<sup>16)</sup> The calculations are of the extended Hückel type, with parameters described in Ref.<sup>17)</sup>. The phosphines were modeled by a pseudo-ligand carrying 3s orbitals only.

<sup>17)</sup> R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.* **98**, 7240 (1976).

The calculated lowest energy point on this surface is the square-planar dimer,  $\Theta = \varphi = 0^\circ$ . But it takes little energy to twist this structure towards the geometry observed in the crystal. Thus the point with  $\Theta = 54^\circ$ ,  $\varphi = 27^\circ$  is only 2.9 kcal/mol higher in energy. Throughout the twisting deformation the  $H_2$  unit prefers to remain between the P–Ni–P planes at  $\Theta/2$ . The tetrahedral dimer structure,  $\Theta = 0^\circ$ ,  $\varphi = 90^\circ$  is much higher in energy. The calculations were repeated for critical points, replacing the terminal pseudo ligands by somewhat more realistic  $PH_3$  groups. The following relative energies were obtained:

"square-planar"	$\Theta = 0^\circ$ , $\varphi = 0^\circ$	[0] kcal/mol
near experimental	$\Theta = 54^\circ$ , $\varphi = 27^\circ$	1.7
"tetrahedral"	$\Theta = 0^\circ$ , $\varphi = 90^\circ$	46.0

We conclude that the dihydride as an isolated molecule would prefer a square-planar structure but that it possesses a very soft potential energy surface for twisting motion which results in the geometry observed in the crystal. Of course the real phosphine ligands are considerably more elaborate than the  $PH_3$  groups used in our calculation. A twisting of the observed structure into a "square-planar dimer" geometry leads to several unacceptable close contacts. Thus we feel that there is no conflict between the computed preference of the idealized dimer and the actual solid state structure of **1**.

We have recently carried out an extensive analysis of the electronic structure of  $M_2L_6$  dimers<sup>17)</sup>. Molecule **1** is unusual in a number of ways, with at least two features requiring explanation: 1. Why is the structure closer to the square-planar rather than the tetrahedral dimer extreme?  $d^9$  examples of the latter are to be found in  $(NO)_2FeX_2Fe(NO)_2$ ,  $X = I^{18)}$ ,  $SEt^{19)}$ , and  $P(CF_3)_2^{20)}$  and  $(CO)_2Ni(PPh_2)_2Ni(CO)_2^{21)}$ . Still another alternative structural type is provided by the unbridged  $Ni_2(CN)_6^{4-}$  and related compounds<sup>22)</sup>. 2. Why is it so easy to twist the  $P_2Ni$  planes relative to each other? For instance there are numerous  $Cu_2Cl_6^{2-}$  structures in which the bridging  $CuCl_2Cu$  plane is twisted relative to the planes of the terminal  $CuCl_2$  groups, but those terminal groups remain coplanar<sup>23)</sup>. We proceed to a molecular orbital analysis of the question, drawing heavily on our previous discussion of  $M_2L_6$  systems<sup>17)</sup>.

<sup>18)</sup> L. F. Dahl, E. Rodulfo de Gil, and R. D. Feltham, *J. Am. Chem. Soc.* **91**, 1653 (1969).

<sup>19)</sup> J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Crystallogr.* **11**, 604 (1958).

<sup>20)</sup> W. Clegg, Univ. of Newcastle, England, private communication. We are grateful to J. K. Burdett for bringing this work to our attention.

<sup>21)</sup> J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc. A* **1970**, 1867.

<sup>22)</sup> O. Jarchow, *Z. Anorg. Allg. Chem.* **383**, 40 (1971); *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **136**, 122 (1973); O. Jarchow, H. Schulz, and R. Nast, *Angew. Chem.* **82**, 43 (1970); *Angew. Chem., Int. Ed. Engl.* **9**, 71 (1970). Similar structures are observed for  $Pt_2Cl_4(CO)_2^{2-}$  and  $Pd_2(CNCH_3)_6^{2+}$ : A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.* **1975**, 1516; D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg, and J. S. Miller, *J. Am. Chem. Soc.* **97**, 1961 (1975).

<sup>23)</sup> S. C. Abrahams and H. J. Williams, *J. Chem. Phys.* **39**, 2923 (1963); P. H. Vossos, D. F. Fitzwater, and R. E. Rundle, *Acta Crystallogr.* **16**, 1037 (1963); R. D. Willett, C. Dwiggins, Jr., R. T. Kruh, and R. E. Rundle, *J. Chem. Phys.* **38**, 2429 (1963); R. D. Willett, *J. Chem. Phys.* **44**, 39 (1966); *J. Chem. Soc., Chem. Commun.* **1973**, 607; R. D. Willett and C. Chow, *Acta Crystallogr., Sect. B* **30**, 207 (1974). For some related Cl bridged  $Cu^I$  structures see: R. D. Willett and R. E. Rundle, *J. Chem. Phys.* **40**, 838 (1962). In the  $Cu^I$  systems the p combinations **6** and **7** are not as low-lying as they are here, being destabilized by the  $\pi$ -donor substituents which characterize these complexes.

A correlation diagram for a concerted conversion of a tetrahedral into a square-planar  $P_2NiH_2NiP_2$  dimer is given on the left side of Figure 2. The level controlling the conformation change is  $b_{2u}$  at left, correlating with  $b_{3u}$  at right.

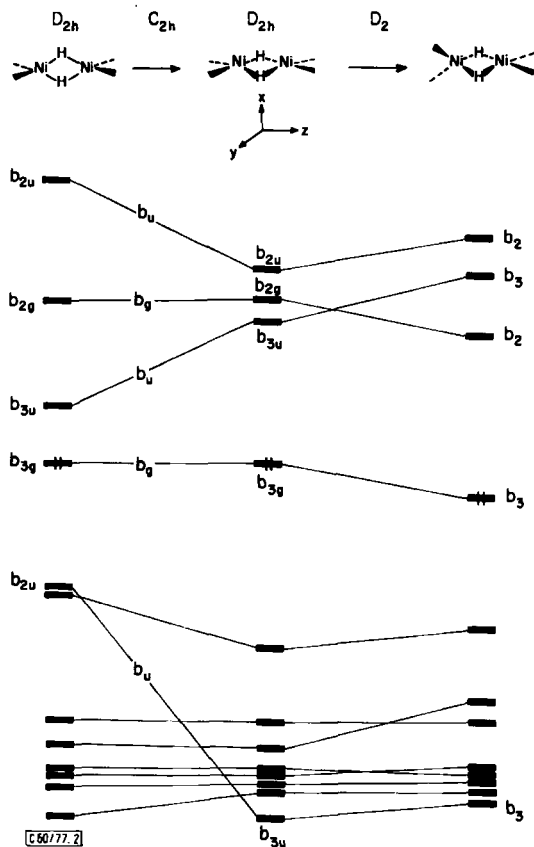
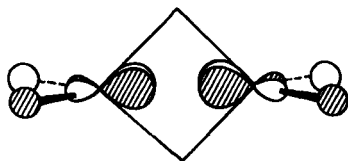


Fig. 2. Correlation diagram for twisting from a tetrahedral  $P_2NiH_2NiP_2$  dimer (left) to a square-planar one (middle).  $C_{2h}$  symmetry is maintained. At right the square-planar dimer is twisted in an opposite sense, maintaining  $D_2$  symmetry. The highest occupied molecular orbital is indicated by small vertical lines. This drawing is not to scale, with the energy scale greatly expanded for the three unfilled orbitals

These orbitals are shown in 3 and 4. 3 is metal-terminal ligand antibonding, somewhat destabilized. 4 doesn't mix with the terminal ligands, and that puts it at low energy.



3  $b_{2u}$

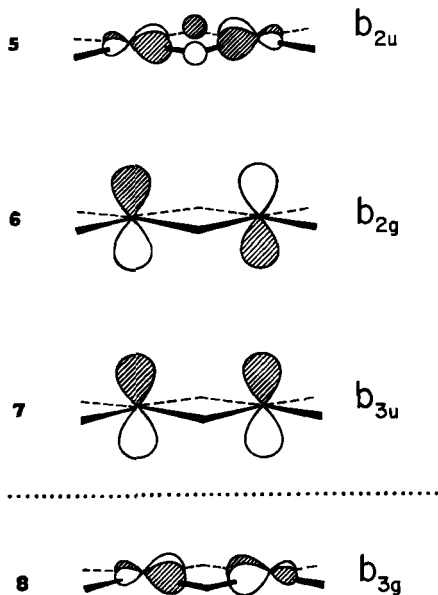


4  $b_{3u}$

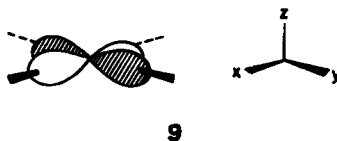


It should be noted that the situation is very different for  $d^9$  dimers in which the bridging groups are halide or phosphido. In these, analyzed in detail elsewhere<sup>17)</sup>, the level ordering is basically different and the tetrahedral geometry is preferred.

An interesting feature of the hydrido-bridged dimer, one connected with both the low-spin ground state of  $P_2NiH_2NiP_2$  and the calculated ease of its deformation from the square-planar geometry, is the nature of its highest occupied and lower unoccupied orbitals. These are shown in 5–8.



The  $b_{2u}$  and  $b_{3g}$  orbitals 5 and 8 are the expected highest-lying members of the d block, symmetric and antisymmetric combinations of the " $x^2 - y^2$ " orbitals of a square-planar monomer, 9.



The ordering  $b_{3g}$  below  $b_{2u}$  is consistent with the interactions allowed with the orbitals of the bridging hydrides. These interact only with  $b_{2u}$ , destabilizing it. This is very important, for, if the bridging ligands were not hydrides but halides, then both  $b_{2u}$  and  $b_{3g}$  would be destabilized by the bridging orbitals. A lesser splitting between the two orbitals would result, with a likely high-spin ground state. This is what happens in many  $Cu^{II}$  dimers<sup>24)</sup>.

<sup>24)</sup> P. J. Hay, J. C. Thibault, and R. Hoffmann, *J. Am. Chem. Soc.* **97**, 4884 (1975).

There are two further low-lying empty orbitals, 6 and 7. These combinations of metal p functions are at unusually low energy in this complex because there are no  $\pi$ -donor substituents to stabilize them. They play an important role in being responsible for the soft potential energy surface for twisting. Fig. 2 shows at right a correlation diagram for twisting from the square-planar dimer along the sense defined in 2. This reduced the molecular symmetry from  $D_{2h}$  to  $D_2$ . The only orbital which drops in energy is the  $b_3$  level descended from the highest occupied molecular orbital, 8. This orbital is stabilized with the lowest unoccupied orbital of the square-planar dimer, 7. Both orbitals transform as  $b_3$  in the reduced  $D_2$  symmetry. The interaction of these two orbitals, with the resultant drop in energy of the occupied  $b_3$  partner, counteracts an increase in energy of some of the lower orbitals. The net result is a total energy that varies little with dihedral angle <sup>25)</sup>.

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Supplementary Material Available: structure factor amplitudes and atomic thermal parameters.

<sup>25)</sup> A still more complicated distortion, yet one carrying the elements of the distortion observed in our case, occurs for  $(PPh_3)_2Rh(CO)_2Rh(PPh_3)_2$ : P. Singh, C. B. Damman, and D. J. Hodgson, *Inorg. Chem.* **12**, 1335 (1973). Synthesis: D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A* **1968**, 2660.

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