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Crystal and molecular structure of 2,3- η^2 -(1,4-dimethoxybut-2-yne)bis(tricyclohexylphosphane)nickel(0), $(\text{Cy}_3\text{P})_2\text{Ni}(\text{MeOCH}_2\text{C}\equiv\text{CCH}_2\text{OMe})$; influence of phosphane ligands on acetylene complexation in nickel(0) complexes

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Abstract

The crystal and molecular structure of 2,3- η^2 -(1,4-dimethoxybut-2-yne)bis(tricyclohexylphosphane)nickel(0) has been determined by an X-ray diffraction study. The complex crystallizes in the triclinic space group $P\bar{1}$ with a 10.523(4), b 11.740(2), c 19.070(5) Å, α 85.21(2), β 86.44(3), γ 65.16(2)°, $Z = 2$. The structure was solved by the heavy-atom method and refined to $R = 0.044$. The coordination geometry at the nickel atom is trigonal-planar. The structure of $(\text{Cy}_3\text{P})_2\text{Ni}(\text{MeOCH}_2\text{C}_2\text{CH}_2\text{OMe})$ is compared with that of the previously described triphenylphosphane analog $(\text{Ph}_3\text{P})_2\text{Ni}(\text{MeOCH}_2\text{C}_2\text{CH}_2\text{OMe})$. The influence of different phosphane ligands on acetylene complexation in nickel(0) complexes is discussed.

Introduction

The structure of the triphenylphosphane complex, $(\text{Ph}_3\text{P})_2\text{Ni}(\text{MeOCH}_2\text{C}_2\text{CH}_2\text{OMe})$ (I) [1] has been described. In addition we recently reported the results of our studies of acetylene activation upon complexation in nickel(0) complexes $\text{L}_2\text{Ni}(\text{YC}_2\text{Y})$ [2,3]. The studies showed correlations between the stretching frequencies $\nu(\text{C}\equiv\text{C})$ and electronic factors of ligands L and between the frequency shift

$\Delta\nu(\text{C}\equiv\text{C})$ resulting from complexation and electronic effects of acetylene substituents Y [3]. These correlations were consistent with the Dewar–Chatt–Duncanson bonding theory [4–7]. For example the increase of Lewis basicity of the ligands L on going from Ph_3P to Cy_3P decreases the $\nu(\text{C}\equiv\text{C})$ from 1826 to 1774 cm^{-1} in the complexes $\text{L}_2\text{Ni}(\text{MeOCH}_2\text{C}_2\text{CH}_2\text{OMe})$. This is probably the result of increased electron density transfer to the alkyne π^* orbitals in the cyclohexyl derivative which would lower the triple-bond order. Studies carried out on a series of platinum complexes $\text{L}_2\text{Pt}(\text{F}_3\text{CC}_2\text{CF}_3)$ by Payne et al. for $\text{L} = \text{Ph}_3\text{P}$, Ph_2CyP , PhCy_2P , and Cy_3P led them to conclude that the main cause of structural variation is steric, rather than electronic [8–10]. It is of interest to discuss the influence of electron donor properties on acetylene complexation in nickel(0) complexes in terms of the correlations between the reactivity parameters, infrared absorption frequencies and structural details of the bonding we found previously [11].

Experimental

The complex $(\text{Cy}_3\text{P})_2\text{Ni}(\text{MeOCH}_2\text{C}_2\text{CH}_2\text{OMe})$ (II) was prepared by the published procedure [3] as follows: A suspension of 2.75 g (10 mmol) $\text{Ni}(\text{cod})_2$, 5.60 g (20 mmol) Cy_3P and 1.14 g (10 mmol) $\text{MeOCH}_2\text{C}_2\text{CH}_2\text{OMe}$ in 50 ml tetrahydrofuran at -78°C was stirred for 1 h with a gradual temperature elevation from -78 to 20°C and for 30 min with heating from 30 to 40°C . Addition of 50 ml hexane followed by filtration and cooling, gave a yellow crystalline precipitate. Pure yellow crystals were recrystallized from a tetrahydrofuran/hexane mixture. Yield: $\text{C}_{42}\text{H}_{76}\text{NiO}_2\text{P}_2$, 1.10 g (15%).

Table 1

Crystal data

Colour	yellow
Formula	$\text{C}_{42}\text{H}_{76}\text{O}_2\text{P}_2\text{Ni}$
Molecular weight	733.73 g mol^{-1}
Crystal system	triclinic
Space group	$P\bar{1}$
Cell constants	a 10.523(4), b 11.740(2), c 19.070(5) Å α 85.21 (2), β 86.44(3), γ 65.16 (2)°
Volume	2129.5 Å ³
Number of formula units Z	2
Density (calculated) D_c	1.14 g cm^{-3}
Absorption coefficient $\mu(\text{Mo-K}\alpha)$	5.6 cm^{-1}
Unique data measured	8352
Observed data with $I \geq 3\sigma(I)$	4623
R	0.044
R_w	0.057
Rest electron density	0.41(6) e Å^{-3}

X-ray diffraction study of (C₇₃P)₂NiC₆H₁₀O₂ (I)

A single crystal of I on a glass fiber, was mounted in an automatic Enraf–Nonius CAD4 diffractometer ($\lambda(\text{Mo-K}\alpha)$), graphite monochromator, $\theta/2\theta$ scan to $2\theta \leq$

Table 2

Atomic coordinates (e.s.d.'s in parentheses)

Atom	x	y	z
Ni	0.02762(6)	0.02973(5)	0.72025(3)
P1	-0.0164(1)	-0.1392(1)	0.73322(6)
P2	-0.1143(1)	0.18937(9)	0.78053(5)
O1	0.3721(5)	-0.0646(4)	0.5716(2)
O2	0.2267(4)	0.2421(4)	0.7162(2)
C1	0.1809(5)	-0.0188(4)	0.6543(2)
C2	0.1574(4)	0.0886(4)	0.6749(2)
C3	0.2793(6)	-0.1114(5)	0.6053(3)
C4	0.469(1)	0.1477(8)	0.5237(5)
C5	0.2179(5)	0.1819(5)	0.6572(3)
C6	0.3016(7)	0.3184(6)	0.7010(4)
C11	0.0114(5)	-0.2144(4)	0.6480(2)
C12	-0.0055(5)	-0.3379(4)	0.6479(2)
C13	0.0470(6)	-0.3964(5)	0.5768(3)
C14	-0.317(6)	-0.3077(5)	0.5171(3)
C15	-0.0196(7)	-0.1826(5)	0.5159(3)
C16	-0.0692(6)	-0.1213(5)	0.5873(2)
C21	-0.1843(4)	-0.1354(4)	0.7746(2)
C22	-0.1908(5)	0.2595(4)	0.8032(3)
C23	-0.3297(6)	-0.2339(5)	0.8423(3)
C24	-0.4558(6)	-0.1569(6)	0.7977(3)
C25	-0.4491(5)	-0.0338(5)	0.7673(3)
C26	-0.3100(5)	-0.0606(4)	0.7276(3)
C31	0.1159(4)	-0.2677(4)	0.7893(2)
C32	0.1033(5)	-0.2294(4)	0.8658(2)
C33	0.2080(5)	-0.3351(5)	0.9122(2)
C34	0.3588(5)	-0.3726(5)	0.8834(3)
C35	0.3726(5)	-0.4082(4)	0.8078(2)
C36	0.2661(5)	-0.3038(4)	0.7611(2)
C41	-0.2464(4)	0.1692(4)	0.8451(2)
C42	-0.1779(5)	0.0875(4)	0.9106(2)
C43	-0.2804(5)	0.0490(5)	0.9556(3)
C44	-0.4097(6)	0.1638(6)	0.9759(3)
C45	-0.4792(5)	0.2484(5)	0.9111(3)
C46	-0.3745(5)	0.2859(4)	0.8672(3)
C51	-0.0149(4)	0.2570(4)	0.8276(2)
C52	0.1072(5)	0.1543(4)	0.8681(2)
C53	0.2047(5)	0.2086(5)	0.8946(3)
C54	0.1202(6)	0.3186(5)	0.9408(3)
C55	0.0003(6)	0.4204(5)	0.9013(3)
C56	-0.0976(5)	0.3675(4)	0.8730(2)
C61	-0.2304(4)	0.3261(4)	0.7230(2)
C62	-0.1521(5)	0.3861(5)	0.6742(3)
C63	-0.2566(6)	0.4981(5)	0.6296(3)
C64	-0.3457(6)	0.4563(5)	0.5857(3)
C65	-0.4218(5)	0.3936(5)	0.6331(3)
C66	-0.3187(5)	0.2829(4)	0.6787(2)

54°). The crystals are triclinic with a 10.523(3), b 11.740(2), c 19.070(5) Å, α 85.21(2), β 86.44(3), γ 65.16(2)°, space group $P\bar{1}$. The intensities of all reflections were corrected for Lorentz and polarization factors. No absorption correction was applied. 4623 reflections with $I \geq 3.0\sigma(I)$ of a total of 8872 collected at room temperature (23°C) were used in the calculations. The crystallographic data are listed in Table 1. The structure was solved by the heavy-atom method which revealed the position of the nickel atom. The remaining atoms were located in subsequent Fourier syntheses. Hydrogen atoms were located in the difference Fourier syntheses and were taken into account in structure factor calculations but their positions were not refined. The structure was refined anisotropically for all non-hydrogen atoms by least-squares techniques to $R = 0.044$, $R_w = 0.057$. The highest peak in the final difference Fourier had a height of 0.41 eÅ⁻³. The final atomic parameters are listed in Table 2. A table listing the atomic coordinates of H atoms, anisotropic thermal parameters for all atoms and a table of interatomic distances and bond angles for the complex (I) are available from the authors. All calculations were performed by a PDP-11/23 PLUS computer using the SDP-PLUS program package.

Discussion

The molecular structure of the title compound is shown in Fig. 1 together with numbering scheme. Figure 2 shows a stereo plot of the molecule. The molecular packing arrangement is illustrated in Fig. 3. Relevant bond distances and bond angles are given in Table 3. Crystals of I consist of discrete molecules, and show no intermolecular distances shorter than 3.5 Å. The coordination about the nickel atom is trigonal-planar. The dihedral angle between the normals to the planes through P1, Ni, P2 and C1, Ni, C2 is a mere 7.8(5)°. The Ni–P distances are 2.211(1) and 2.204(2) Å. The P1NiP2 angle is 115.14(5)°. The average phosphorus-carbon and the carbon-carbon bond lengths in the cyclohexyl rings are 1.857(4) Å and 1.531(8) Å, respectively. These bond lengths are typical for the tricyclohexylphosphane nickel moiety [12]. All the cyclohexyl rings show the chair conformation. The alkyne

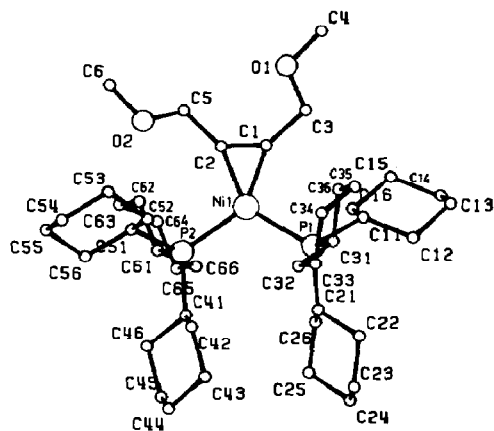


Fig. 1. The structure of 2,3- η^2 -(1,4-dimethoxybut-2-yne)bis(tricyclohexylphosphane)nickel(0) (I) with numbering scheme.

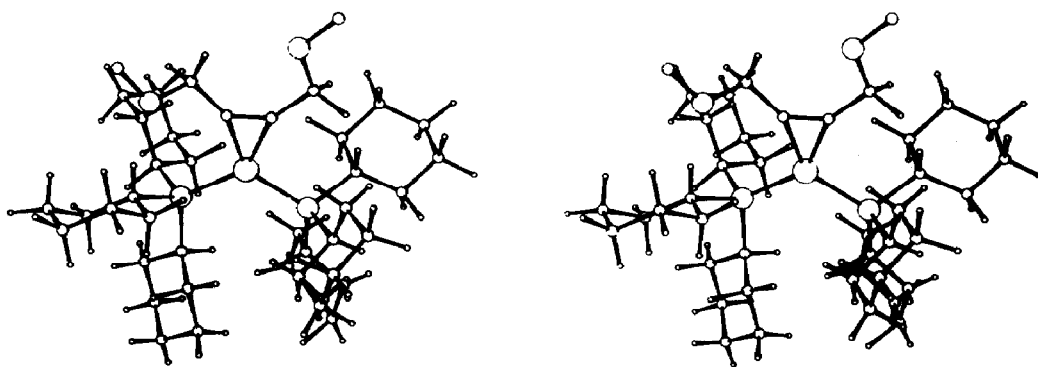


Fig. 2. Stereo plot of I.

ligand is coordinated “side-on” at the carbon–carbon triple bond. The nickel–alkyne C distances are almost equal (1.899(4) and 1.907(5) Å). The C1NiC2 angle is 39.0(3)°. The coordinated alkyne is no longer linear but displays *cis* geometry. The deviations from linearity (bond angles C1C2C5 and C2C1C3 are 134.9(4) and 138.8(5)°, respectively) are characteristic for η -coordinated alkynes [13]. The C1–C2 distance of 1.271(7) Å lies between that for normal C≡C (1.20 Å) and C=C bonds (1.34 Å).

Influence of ligands

The data of Table 4 show that the acetylenic triple bond in $(\text{Cy}_3\text{P})_2\text{Ni}(\text{MeOCH}_2\text{C}_2\text{CH}_2\text{OMe})$ 1.271(7) Å is slightly longer than in its Ph_3P analogue $(\text{Ph}_3\text{P})_2\text{Ni}(\text{MeOCH}_2\text{C}_2\text{CH}_2\text{OMe})$ (II) [1] 1.261(4) Å ($\Delta < 6\sigma$).

The Ni–C bond distances in the two complexes are almost identical, but the Ni–P bond distances (2.211(1) and 2.204(2) Å) in the Cy_3P complex (I) are longer than those in the Ph_3P complex (II) (2.1585(7) and 2.1561(5) Å).

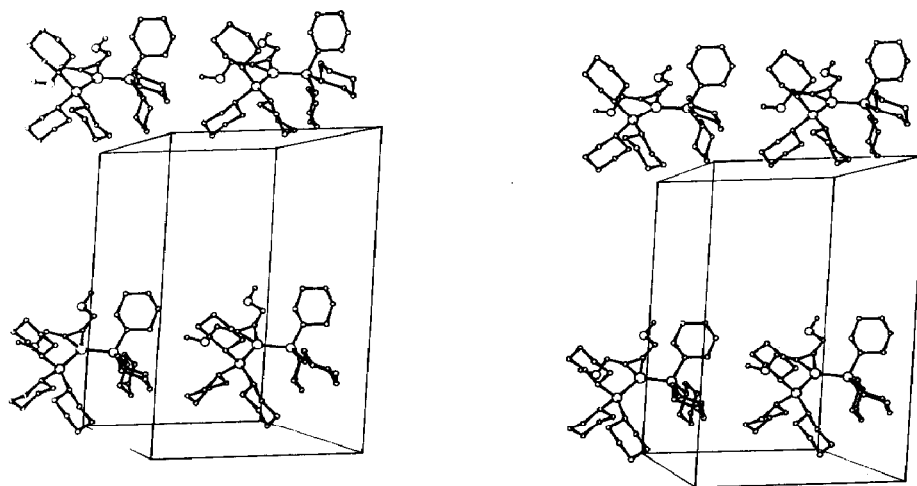


Fig. 3. Molecular packing in the crystal of I.

Table 3

Relevant bond distances (Å) and angles (°) of I

Ni-P1	2.211(1)	P1-Ni-P2	115.14(5)
Ni-P2	2.204(2)	P1-Ni-C1	102.5(2)
Ni-C1	1.899(4)	P1-Ni-C2	141.2(1)
Ni-C2	1.907(5)	P2-Ni-C1	142.4(2)
P1-C11	1.863(4)	P2-Ni-C2	103.6(1)
P1-C21	1.874(5)	C1-Ni-C2	39.0(3)
P1-C31	1.873(4)	Ni-P1-C11	110.6(2)
P2-C41	1.877(5)	Ni-P1-C21	122.3(1)
P2-C51	1.861(5)	Ni-P1-C31	111.7(2)
P2-C61	1.871(4)	Ni-P2-C41	119.8(1)
O1-C3	1.408(8)	Ni-P2-C51	111.3(1)
O1-C4	1.423(9)	Ni-P2-C61	112.8(1)
O2-C5	1.405(8)	C3-O1-C4	113.4(7)
O2-C6	1.43(2)	C5-O2-C6	112.6(5)
C1-C2	1.271(7)	Ni-C1-C2	79.9(3)
C1-C3	1.494(6)	Ni-C1-C3	150.3(4)
C2-C5	1.489(8)	C2-C1-C3	138.8(5)
C11-C12	1.534(8)	Ni-C2-C1	70.1(3)
C11-C16	1.543(6)	Ni-C2-C5	154.9(3)
C12-C13	1.536(7)	C1-C2-C5	134.9(4)
C13-C14	1.503(7)	O1-C3-C1	110.1(5)
C14-C15	1.52(1)	O2-C5-C5	112.7(4)
C15-C16	1.550(7)		

Bend-back angles of 30.9(2) and 33.0(3)° in the complex (II) are increased to 41.2(5) and 45.1(4)° on replacement of Ph₃P by Cy₃P in the complex (I). This finding is in good agreement with the results reported by Payne et al. for

Table 4

Parameters for L₂Ni(MeOCH₂C₂CH₂OMe)

L	Ph ₃ P (II)	Cy ₃ P (I)
electronic param. χ (cm ⁻¹) [15]	12.9	0.3
steric parameter θ (°) [15]	145	170
$\Delta\nu(\text{C}\equiv\text{C})$ (cm ⁻¹)	438	490
Distances (Å)		
C-C	1.261(4)	1.271(7)
Ni-C	1.896(2)	1.899(4)
	1.897(3)	1.907(5)
Ni-P	2.1585(7)	2.211(1)
	2.1561(5)	2.204(2)
Angles (°)		
C-C-CH ₂ OMe	149.1(2)	134.9(4)
	147.0(3)	138.8(5)
bend-back	30.9(2)	45.1(4)
	33.0(3)	41.2(5)
C-Ni-C	38.82(9)	39.0(3)
P-Ni-P	117.82	115.13
dihedral CNiC/PNiP	2.8(5)	7.8(5)

Table 5

Parameters [8–10,15] for $L_2Pt(F_3CC_2CF_3)$

L	Ph ₃ P	Ph ₂ CyP	PhCy ₂ P	Cy ₃ P
electronic param. χ (cm ⁻¹)	12.9	8.7	4.5	0.3
steric parameters θ (°) [15]	145	–	–	170
$\Delta\nu(C\equiv C)$ (cm ⁻¹)	525	550	560	570
Distances (Å)				
C–C	1.255(9)	1.294(14)	1.294(16)	1.260(10)
Ni–C	2.024(5)	2.039(7)	2.048(12)	2.047(7)
	2.031(5)	–	2.022(12)	2.045(8)
Ni–P	2.277(1)	2.297(1)	2.292(3)	2.309(2)
	2.285(1)	–	2.287(3)	2.301(2)
Angles (°)				
bend-back	39.3(6)	43.5(5)	40(1)	46.3(8)
	40.4(6)	–	47(1)	44.6(8)
C–Pt–C	36.1(2)	37.0(4)	37.1(4)	39.9(3)
P–Pt–P	100.17(4)	100.77(8)	108.6(1)	110.23(6)
dihedral CPtC/PPtP	3.7(4)	1.4(2)	3.7(8)	6.5(5)

$L_2Pt(F_3CC_2CF_3)$ (Table 5) complexes, in which the alkyne ligand bend-back angles do vary significantly. The authors suggested that these variations were due to steric effects [8].

In general it is not known whether steric effects of ligands act in conjunction with or opposite to electronic effects. Further studies on the structural influence of ligands in nickel(0) complexes with acetylenes on acetylene complexation should elucidate the well documented activation of acetylenes in some reactions when strong σ -donor ligands are used [2,3,14]. Thus future studies on which structural peculiarities most directly influence chemical reactivity should be performed. The following possibilities are suggested:

- (i) longer C–C triple bond distances;
- (ii) longer Ni–P bonds (which favors a better ligand dissociation);
- (iii) larger bend-back angles;
- (iv) any combination of these factors.

Our structural data show that alkyne distortion in nickel(0) complexes with a donor ligand such as Cy₃P is higher than in its phenyl analogue. This effect is associated with higher reactivity in some reactions [2,3,14].

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