Journal of Organometallic Chemistry, 389 (1990) 409–416
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20652

Crystal and molecular structure of 2,3-η^2-(1,4-dimethoxybut-2-yne) bis(triphenylphosphane)nickel(0), $(Ph_3P)_2Ni(MeOCH_2C{\equiv}CCH_2OMe)$; influence of acetylene substituents on acetylene complexation in nickel(0) complexes

U. Rosenthal, G. Oehme,

Academy of Sciences of GDR, Central Institute of Organic Chemistry, Division of Complex Catalysis, Buchbinderst. 5–6, Rostock 1 (GDR-2500)

H. Görls,

Friedrich-Schiller-University, Section of Physics, Max-Wien-Pl. 1, Jena (GDR-6900)

V.V. Burlakov, A.V. Polyakov, A.I. Yanovsky, and Yu.T. Struchkov

Institute of Organo-Element Compounds of the USSR Academy of Sciences, Vavilov St. 28, Moscow 117813 (USSR)

(Received December 20th, 1989)

Abstract

The crystal and molecular structure of 2,3-η^2-(1,4-dimethoxy-but-2-yne)bis(triphenylphosphane)nickel(0) has been determined by an X-ray diffraction study. The complex crystallizes in the triclinic space group $P\bar{1}$: a 11.478(1), b 11.882(1), c 15.250(2) Å, α 67.25(1), β 87.55(1) and γ 71.27(1)°, $Z = 2$. The structure was solved by the heavy-atom method and refined to $R = 0.034$. The coordination geometry at the nickel atom is trigonal-planar. The structure of $(Ph_3P)_2Ni(MeOCH_2C_2CH_2OMe)$ has been compared with those previously described for $(Ph_3P)_2Ni(Me_3SiC_2SiMe_3)$ and $(Ph_3P)_2Ni(MeOOCC_2COOMe)$. The influence of electronic factors of acetylene substituents on acetylene complexation in nickel(0) complexes is discussed.

Introduction

The structures of the acetylene complexes, $(Ph_3P)_2Ni(Me_3SiC_2SiMe_3)$(II) [1] and $(Ph_3P)_2Ni(MeCOOC_2COOMe)$(III) [2], have been described. In addition, we recently reported the results of our studies of activation of acetylenes upon complexation in nickel(0) complexes $L_2Ni(YC_2Y)$ [3,4]. From these studies a correlation was

0022-328X/90/$03.50

found to exist between stretching frequencies $\nu(C{\equiv}C)$ and electronic factors of ligands L and between the frequency shift $\Delta\nu(C{\equiv}C)$ resulting from the complexation and inductive parameters σ_I of acetylene substituents Y [4]. Later it was also found that there is a correlation between reactivity, infrared absorption frequencies and structural parameters in nickel(0) acetylene complexes [5]. Variations within the series of our nickel(0) complexes are consistent with the Dewar–Chatt–Duncanson bonding theory [6–9]. For example, replacement of the Me_3Si group in $(Ph_3P)_2Ni(Me_3SiC_2SiMe_3)$ by a more electronegative group such as MeOOC in $(Ph_3P)_2Ni(MeOOCC_2COOMe)$ would lower the triple-bond order as a result of an increase in transfer of electron density to the π^*-orbitals. Earlier studies by D.H. Farrar and N.C. Payne [10] of platinum analogs led them to conclude that X-ray diffraction is a poor method for detecting small differences in acetylene complexation. Thus it was of interest to study the influence of the electronic factors of acetylene substituents on acetylene complexation in nickel(0) complexes and the relationships between the spectroscopic and structural parameters.

Experimental

The complex $(Ph_3P)_2Ni(MeOCH_2C_2CH_2OMe)$ (I) was prepared by a published procedure [14]. Yellow crystals were obtained by recrystallization from tetrahydrofuran/hexane mixtures.

X-Ray diffraction study of $[(Ph)_3P]_2NiC_6H_{10}O_2$ *(I)*

A single crystal of I mounted on a glass fiber, was mounted in an automatic Enraf–Nonius CAD4 diffractometer (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$ scanning to $2\theta \leq 58°$). The crystals are triclinic, space group $P\bar{1}$, a 11.478(1), b 11.882(1), c 15.250(2) Å, α 67.25(1), β 87.55(1), γ 71.27(1)°, $Z = 2$. At room

Table 1

Crystal data

Colour	yellow
Formula	$C_{42}H_{40}O_2P_2Ni$
Molecular weight	697.44 g mol^{-1}
Crystal system	triclinic
Space group	$P\bar{1}$
Cell constants	a 11.478(1) Å, b 11.882(1) Å, c 15.250(2) Å α 67.25 (1)°, β 87.55 (1)°, γ 71.27 (1) °
Volume	1808.7 $Å^3$
Number of formula units, Z	2
Density (calculated) D_c	1.28 g cm^{-3}
Absorption coefficient μ(Mo-K_α)	6.6 cm^{-1}
Unique data measured	8601
Observed data with $I \geq 3\sigma(I)$	6035
R	0.034
R_w	0.046
Rest electron density	0.57(6) e $Å^{-3}$

temperature 9078 reflections were measured, of which 8601 were unique. No absorption correction was applied. After averaging, 4623 reflections with $I \geq 3.0\sigma(I)$ were used in the calculations. The crystallographic data are listed in Table 1. The

Table 2

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

Atom	x/a	y/b	z/c
Ni	0.23767(2)	−0.00137(2)	0.28282(2)
P1	0.31545(5)	−0.17158(5)	0.25171(4)
P2	0.16687(5)	0.18274(5)	0.16397(4)
O1	0.3729(2)	−0.1903(2)	0.5769(1)
O2	0.1695(2)	0.1462(2)	0.5061(2)
C1	0.2635(2)	−0.0731(2)	0.4180(2)
C2	0.2149(2)	0.0480(2)	0.3883(2)
C3	0.3143(3)	−0.1988(3)	0.5024(2)
C4	0.4815(6)	−0.1610(7)	0.5486(3)
C5	0.1632(3)	0.1653(3)	0.4098(2)
C6	0.1072(5)	0.0691(4)	0.5609(3)
C11	0.4752(2)	−0.2488(2)	0.3053(2)
C12	0.5414(2)	−0.1662(3)	0.2962(2)
C13	0.6622(3)	−0.2140(3)	0.3390(2)
C14	0.7157(3)	−0.3448(4)	0.3914(3)
C15	0.6522(3)	−0.4249(3)	0.4008(3)
C16	0.5317(3)	−0.3797(3)	0.3584(2)
C21	0.2400(2)	−0.2950(2)	0.3027(2)
C22	0.1437(2)	−0.2743(2)	0.3580(2)
C23	0.0791(3)	−0.3611(3)	0.3931(2)
C24	0.1106(3)	−0.4696(3)	0.3727(2)
C25	0.2075(3)	−0.4922(3)	0.3179(2)
C26	0.2713(2)	−0.4055(2)	0.2819(2)
C31	0.3278(2)	−0.1713(2)	0.1309(2)
C32	0.2185(3)	−0.1270(3)	0.0735(2)
C33	0.2208(3)	−0.1283(3)	−0.0172(2)
C34	0.3318(3)	−0.1707(3)	−0.0522(2)
C35	0.4403(3)	−0.2129(3)	0.0032(2)
C36	0.4398(2)	−0.2138(3)	0.0954(2)
C41	0.1466(2)	0.1999(2)	0.0400(2)
C42	0.2522(2)	0.1563(2)	−0.0022(2)
C43	0.2445(3)	0.1667(3)	−0.0956(2)
C44	0.1297(3)	0.2195(3)	−0.1468(2)
C45	0.0251(3)	0.2618(3)	−0.1062(2)
C46	0.0319(2)	0.2535(2)	−0.0125(2)
C51	0.2584(2)	0.2901(2)	0.1456(2)
C52	0.2328(2)	0.4076(2)	0.0659(2)
C53	0.3077(3)	0.4826(3)	0.0527(2)
C54	0.4087(3)	0.4432(3)	0.1162(2)
C55	0.4360(3)	0.3275(3)	0.1944(2)
C56	0.3606(2)	0.2507(2)	0.2093(2)
C61	0.0123(2)	0.2712(2)	0.1848(2)
C62	−0.0256(3)	0.3970(2)	0.1785(2)
C63	−0.1429(3)	0.4518(3)	0.2029(3)
C64	−0.2212(3)	0.3815(3)	0.2334(2)
C65	−0.1854(3)	0.2567(3)	0.2391(2)
C66	−0.0695(2)	0.2015(3)	0.2162(2)

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 included in the structure factor calculations but their positions were not refined. The structure was refined anisotropically for non-hydrogen atoms by least-squares technique in to $R = 0.034$, $R_w = 0.046$. The highest peak in the final difference Fourier had a height of 0.57 eÅ^{-3}. The final atomic parameters are listed in Table 2. Tables listing the atomic coordinates of H atoms, the anisotropic thermal parameters for other atoms and the interatomic distances and bond angles for I are available from the authors. All calculations were performed with a PDP-11/23 PLUS computer using SDP-PLUS program package.

Discussion

The molecular structure of I is shown in Fig. 1 together with the numbering scheme. Figure 2 depicts a stereo plot of the molecule. The molecular packing arrangement is illustrated in Fig. 3. The relevant bond distances and bond angles are given in Table 3. The structure consists of discrete molecules.

In the crystal there are 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 small, viz., 2.8(5)°. The Ni–P distances are 2.1585(7) and 2.1561(5) Å. The P1NiP2 angle is 117.82(3)°. The average phosphorus–carbon and the carbon–carbon bond lengths in the phenyl rings are 1.831(2) and 1.385(5) Å respectively. These bond lengths are typical for the triphenylphosphane nickel moiety [11]. Both the triphenylphosphane ligands have a propeller conformation, which corresponds to a minimal steric hindrance. The alkyne ligand is coordinated "side-on" at the carbon–carbon triple bond. The nickel–alkyne C distances are quite similar, 1.896(2) and 1.897(3) Å. The C1NiC2 angle is equal to 38.82(9)°. The coordinated alkyne is no longer linear but displays a *cis* geometry. The deviations from linearity (bond angles C1C2C5 and C2C1C3 are

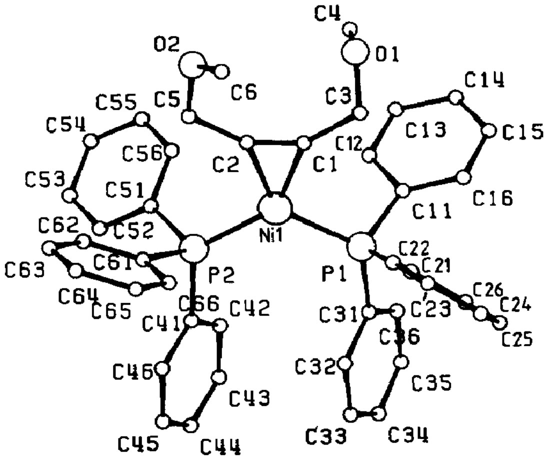

Fig. 1. The structure of 2,3-η^2-(1,4-dimethoxy-but-2-yne)bis(triphenylphosphane)nickel(0) (I) with numbering scheme.

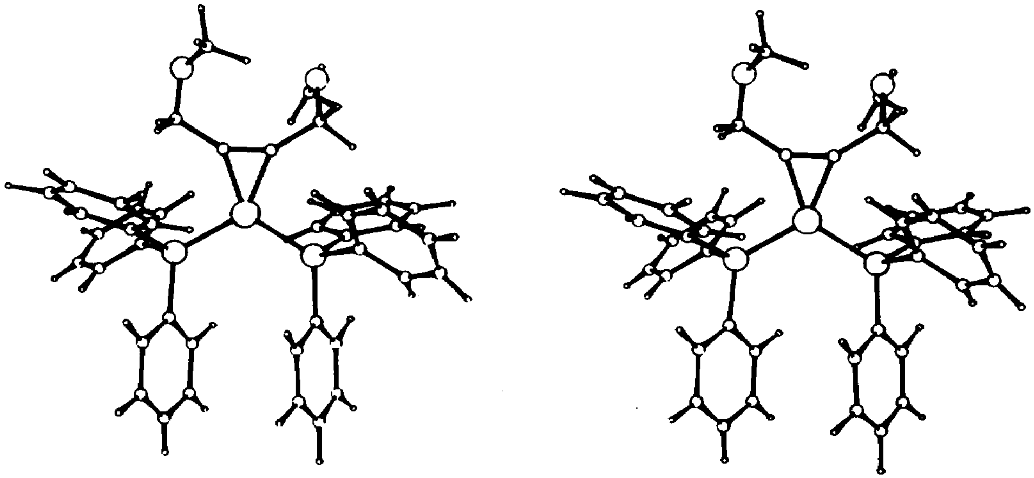

Fig. 2. Stereo plot of I.

149.1(2)° and 147.0(3)°, respectively) are characteristic of η-coordinated alkynes [12]. The C1–C2 distance of 1.261(4) Å lies between the distances of normal C≡C bonds (1.20 Å) and C=C bonds (1.34 Å).

Influence of the acetylene substituents

The data of Table 4 indicate a particular trend in the acetylenic C–C bond distances, however the differences in the bond lengths 1.256(2) Å in $(Ph_3P)_2Ni(Me_3SiC_2SiMe_3)$ (II), 1.261(4) Å in $(Ph_3P)_2Ni(MeOCH_2C_2CH_2OMe)$ (I) and 1.279(8) Å in $(Ph_3P)_2Ni(MeOOCC_2COOMe)$ (III) is scarcely significant ($\Delta < 6\sigma$). Nevertheless such a trend is understandable in terms of the Dewar–Chatt–Duncanson bonding theory which implies that electron-withdrawing properties of the acetylene substituents decrease with effective triple-bond order. The shortening

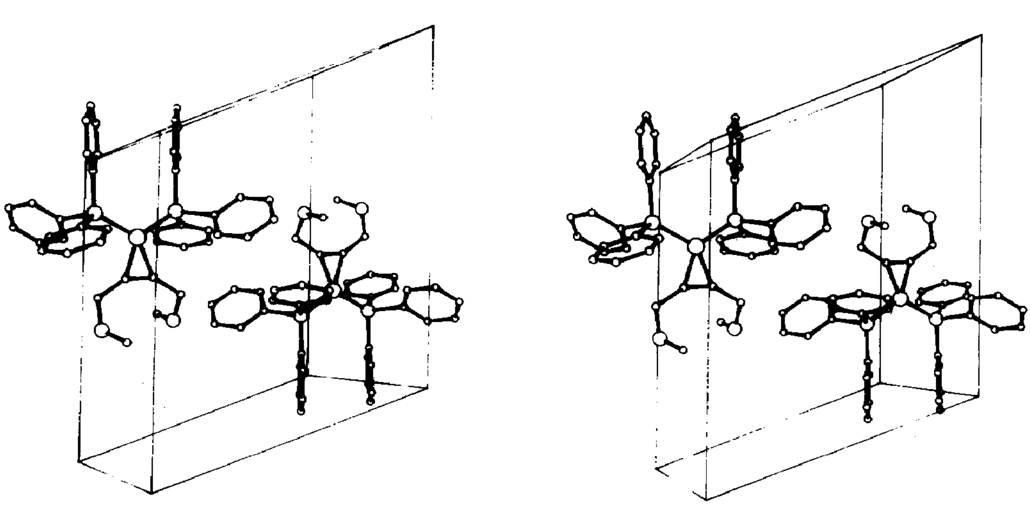

Fig. 3. Molecular packing in the crystal of I.

Table 3

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

Ni-P1	2.1585(7)	P1-Ni-P2	117.82(3)
Ni-P2	2,1561(5)	P1-Ni-C1	101,42(8)
Ni-Cl	1.896(2)	P1-Ni-C2	140,20(6)
Ni-C2	1.897(3)	P2-Ni-C2	101,89(6)
P1-C11	1.827(2)	C1-Ni-C2	38,82(9)
P1-C21	1.839(3)	Ni-P1-C11	107.3(1)
P1-C31	1.840(3)	Ni-P1-C21	114.95(8)
P2-C41	1.838(2)	Ni-P1-C31	124.85(7)
P2-C51	1.835(3)	C3-O1-C4	110,4(3)
P2-C61	1.835(2)	C5-O2-O6	114.3(4)
O1-C3	1.396(4)	Ni-C1-C2	70.6(1)
O1-C4	1.407(8)	Ni-C1-C3	142.4(2)
O2-C5	1.398(4)	C2-C1-C3	147.0(3)
O2-C6	1.352(6)	Ni-C2-C1	70.6(2)
C1-C2	1.261(4)	Ni-C2-C5	140.4(2)
C1-C3	1.499(3)	C1-C2-C5	149.1(2)
C2-C5	1.486(4)	O1-C3-C1	114.3(3)
C11-C12	1.387(5)	O2-C5-C2	116.4(2)
C11-C16	1.385(3)	P1-C11-C12	115.9(2)
C12-C13	1.399(4)	P1-C11-C16	125.8(2)
C13-C14	1.379(5)		
C14-C15	1.337(6)		
C15-C16	1.398(5)		

Table 4

Spectroscopic and geometric parameters of $(Ph_3P)_2Ni(YC_2Y)$

	(II) [1]	(I)	(III) [2]
YC_2Y	$Me_3SiC_2SiMe_3$	$MeOCH_2C_2CH_2OMe$	$MeOOCC_2COOMe$
$\sigma_I(Y)$ [a] [15]	−0.11	+0.11	+0.32
$\Delta\nu(C\equiv C)$ (cm^{-1})	370	438	449
$\Delta\delta$(C-C) (ppm)	38.76	41.11	55.10
distances (Å)			
C-C	1.256(2)	1.261(4)	1.279(8)
Ni-C	1.927(2)	1.896(2)	1.848(6)
		1.897(3)	1.878(7)
Ni-P	2.172(1)	2.1585(7)	2.184(2)
		2.1561(5)	2.182(2)
angles (°)			
C-C-Y	143.3(1)	149.1(2)	144.7(7)
		147.0(3)	137.9(6)
bend-back	36.7(1)	30.9(2)	35.3(7)
		33.0(3)	42.1(6)
C-Ni-C	38.14(7)	38.82(9)	40.1(2)
P-Ni-P	112.04	117.82	109.51
dihedral, CNiC/PNiP	27.3	2.8(5)	9.7(5)

[a] Inductive parameter.

Table 5

Spectroscopic and geometric parameters of $(Ph_3P)_2Pt(YC_2Y)$ [10]

YC_2Y	PhC_2Ph	$F_3CC_2CF_3$	NCC_2CN
$\sigma_I(Y)$ (15)	0.12	0.4	0.57
$\Delta\nu(C\equiv C)$ (cm^{-1})	455	525	535
Distances (Å)			
C–C	1.32(9)	1.255(9)	1.40
Pt–C	2.01	2.024(9)	–
	2.06	2.031(5)	–
Pt–P	2.28	2.277(1)	–
	2.27	2.285(1)	–
Angles (°)			
bend-back	40.41	39.9(5)	–
C–Pt–C	39	36.1	–
P–Pt–P	102	100.17(4)	–
dihedral, CPtC/PPtP	14	3.7(4)	8

of the Ni–C bond distances, from 1.927(2) Å (II), to 1.896(2)/1.897(3) Å in (I) and 1.848(6)/1.878(7) Å in (III), and the increase of the CNiC angles in the same series, 38.14(7)° (II), 38.82(9)° (I) and 40.1(2)° (III), are consistent with the Dewar–Chatt–Duncanson scheme. The differences probably reflect the general trend that the C–C triple bond lengthens as the bend-back angle is increased. However, $(Ph_3P)_2Ni(Me_3SiC_2SiMe_3)$ (II) is an exception. The effect and the extremely high dihedral angle of 27.3° in II might be caused by the steric crowding because of the bulky Me_3Si groups in II. No correlations between the structural parameters and electron-withdrawing or -releasing properties of the acetylene substituents [13] were found for the platinum analogs $(Ph_3P)_2Pt(YC_2Y)$ (Table 5). Davies and Payne [13] suggested that the bonding by acetylene complexation is relatively insensitive to the nature of the acetylene substituent and geometric differences are too small to be detected. Our study of the nickel(0) complexes $(Ph_3P)_2Ni(YC_2Y)$ also shows only small differences. However, some structural trends can be discerned which reflect the increase of the electron-withdrawing properties of acetylene substituents (lengthening of the coordinated triple C–C bond, shortening of the Ni–C bonds and an increase of the CNiC angles) and which are in good agreement with the generally accepted bonding theory [6–9].

References

1 U. Rosenthal, W. Schulz, H. Görls, Z. Anorg. Allg. Chem. 550 (1987) 169.
2 U. Rosenthal, G. Oehme, H. Görls, V.V. Burlakov, A.V. Polyakov, A.I. Yanovsky, Yu.T. Struchkov, J. Organomet. Chem. 389 (1990) 251.
3 U. Rosenthal, W. Schulz, Z. Chem. 25 (1985) 227.
4 U. Rosenthal, W. Schulz, J. Organomet. Chem. 321 (1987) 103.
5 U. Rosenthal, H. Görls, J. Organomet. Chem. 348 (1988) 135.
6 E.O. Greaves, C.J.L. Lock, P.M. Maitlis, Can. J. Chem. 46 (1968) 3879.
7 J. Chatt, L.A. Duncanson, J. Chem. Soc. (1953) 2939.
8 M.J.S. Dewar, Bull. Soc. Chim. France 18 (1951) C79.
9 J.H. Nelson, K.S. Weelock, L.C. Cusachs, H.B. Jonassen, J. Am. Chem. Soc. 91 (1969) 7005.
10 D.H. Farrar, N.C. Payne, J. Organomet. Chem. 220 (1981) 251.

11 D. Walther, E. Dinjus, H. Görls, J. Sieler, O. Lindqvist, L. Anderson, J. Organomet. Chem. 286 (1985) 193; H. Görls, B. Schulz, U. Rosenthal, W. Schulz, Cryst. Res. Technol., 23 (1988) 25; F.J. Lalor, T.J. Desmond, G. Ferguson, P.Y. Siew, J. Chem. Soc. Dalton Trans. (1982) 1981; W. Keim, F.H. Kowaldt, R. Goddard, C. Krüger, Angew. Chem. 90 (1978) 493; C.D. Cook, Chung Hoe Koo, S.C. Nyburg, M.T. Shiomi, Chem. Comm. (1967) 426.
12 K.R. Pörschke, Y.H. Tsay, C. Krüger, Angew. Chem. 97 (1985) 334; R.S. Dickson, J.A. Ibers, J. Organomet. Chem. 36 (1972) 191; B. Apotecher, Dissertation, Bochum (1983); U. Rosenthal, W. Schulz, H. Görls, Z. Anorg. Allg. Chem. 550 (1987) 169.
13 B.W. Davies, N.C. Payne, J. Organomet. Chem. 99 (1975) 315.
14 U. Rosenthal, Z. Anorg. Allg. Chem. 482 (1981) 179.
15 M. Charton, Progr. Phys. Org. Chem. 13 (1981) 119.