

Journal of Organometallic Chemistry, 389 (1990) 251–258
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20651

Crystal and molecular structure of (η^2 -acetylenedimethyldicarboxylate)bis(triphenylphosphane) nickel(0), $(\text{Ph}_3\text{P})_2\text{Ni}(\text{MeOCC}\equiv\text{CCOOMe})$; influence of metals on acetylene complexation

U. Rosenthal ^{*}, G. Oehme,

*Academy of Sciences of GDR, Central Institute of Organic Chemistry, Division of Complex Catalysis,
Buchbinderstr. 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 (η^2 -acetylenedimethyldicarboxylate)bis(triphenylphosphane)nickel(0) has been determined by an X-ray diffraction study. The complex crystallizes in the monoclinic space group $P2_1/c$ with a 11.704(4), b 15.453(5), c 21.580(5) Å, β 112.98(2)°, $Z = 4$. The structure was solved by the heavy-atom method and refined to $R = 0.058$. The coordination geometry at the nickel atom is trigonal-planar. The structure of $(\text{Ph}_3\text{P})_2\text{Ni}(\text{MeOCC}_2\text{COOMe})$ has been compared with that of a palladium analog $(\text{Ph}_3\text{P})_2\text{Pd}(\text{MeOCC}_2\text{COOMe})$. The influence of the nature of metal in the nickel triad on acetylene complexation is discussed.

Introduction

Many stable monomeric metal(0) complexes of the nickel triad with π -bonded acetylenes have been reported; the platinum complexes are the easiest and those of nickel are the most difficult to isolate [1]. Some years ago Greaves, Lock and Maitlis [2] described their attempts to prepare the dimethylacetylenedicarboxylate complex $(\text{Ph}_3\text{P})_2\text{Ni}(\text{MeOCC}_2\text{COOMe})$. However the only result of their efforts was an

unidentified amorphous yellow complex. We later did succeed in preparing the carboxylate complex [3]. We found that the series of closely related and structurally similar complexes $(\text{Ph}_3\text{P})_2\text{M}(\text{MeOCC}_2\text{COOMe})$ show a decrease in the frequency shift $\Delta\nu(\text{C}\equiv\text{C})$ in the order $\text{Pt} > \text{Ni} > \text{Pd}$; $\Delta\nu(\text{C}\equiv\text{C})$ can be used as a measure of the acetylene C–C bond order [4,5]. This effect was first studied in complexes $(\text{Ph}_3\text{P})_2\text{M}(\text{F}_3\text{CC}_2\text{CF}_3)$ and suggests that the thermal stability of these complexes is mainly governed by backbonding and is reflected in the decrease in infrared frequencies [2,5].

Although many acetylene complexes of the $\text{L}_2\text{Ni}(\text{YC}_2\text{Y})$ type are known, few of their structures have been established from X-ray diffraction [6]. Thus we decided to determine the structure of $(\text{Ph}_3\text{P})_2\text{Ni}(\text{MeOCC}_2\text{COOMe})$ in order to compare it with the structure of the well known palladium analog $(\text{Ph}_3\text{P})_2\text{Pd}(\text{MeOCC}_2\text{COOMe})$ [7]. This study would enable us to examine the structural changes for complexes $(\text{Ph}_3\text{P})_2\text{M}(\text{MeOCC}_2\text{COOMe})$, which occur on going from Pd to Ni. Farrar and Payne [8] have studied the complexes $(\text{Cy}_3\text{P})_2\text{M}(\text{F}_3\text{CC}_2\text{CF}_3)$ with $\text{M} = \text{Pt}, \text{Pd}$ and they concluded that the nature of the metal atom has no bearing on the most important structural parameters.

Experimental

The complex $(\text{Ph}_3\text{P})_2\text{Ni}(\text{MeOCC}_2\text{COOMe})$ (I) was prepared by published methods [3]. The yellow brown crystals were recrystallised from tetrahydrofuran/hexane mixtures.

X-ray diffraction study of $(\text{Ph}_3\text{P})_2\text{NiC}_6\text{H}_6\text{O}_4$ (I)

A single crystal of I, sealed in a glass capillary, was mounted on an automatic Enraf–Nonius CAD4 diffractometer ($\lambda(\text{Mo-}K_\alpha)$, graphite monochromator, $\theta/2\theta$ scan to $2\theta \leq 56^\circ$). Crystals of I are monoclinic: a 11.704(4), b 15.453(5), c

Table 1

Crystal data

Colour	yellow brown
Formula	$\text{C}_{42}\text{H}_{36}\text{NiO}_4\text{P}_2$
Molecular weight	725.41 g mol ⁻¹
Crystal system	monoclinic
Space group	$P2_1/c$
Cell constants	a 11.704(4), b 15.453(5), c 21.580(5) Å β 112.98 (2)°
Volume	3593.3 Å ³
Number of formula units, Z	4
Density (calculated) D_c	1.34 g cm ⁻³
Absorption coefficient $\mu(\text{Mo-}K_\alpha)$	6.7 cm ⁻¹
Unique data measured	8495
Observed data with $I \geq 3\sigma(I)$	2590
R	0.058
R_w	0.065
Rest electron density	1.09(10) e Å ⁻³

Table 2

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

Atom	x	y	z
Ni	0.00440(8)	0.07491(7)	0.21824(5)
P1	-0.1916(2)	0.0850(2)	0.2013(1)
P2	0.1144(2)	0.0558(1)	0.3253(1)
O1	-0.0435(6)	0.1178(5)	0.0208(3)
O2	-0.1624(5)	0.0193(4)	0.0418(3)
O3	0.3125(5)	0.0179(4)	0.1865(3)
O4	0.2800(5)	0.1609(4)	0.1837(3)
C1	0.0027(6)	0.0717(6)	0.1323(3)
C2	0.1154(7)	0.0737(6)	0.1746(4)
C3	-0.0637(7)	0.0725(7)	0.0603(4)
C4	-0.243(1)	0.0182(7)	-0.0288(5)
C5	0.2419(6)	0.0775(7)	0.1819(4)
C6	0.4045(8)	0.1754(8)	0.1883(5)
C11	-0.2878(7)	0.1417(5)	0.1219(4)
C12	-0.4102(8)	0.1177(6)	0.0853(4)
C13	-0.4781(8)	0.1649(7)	0.0283(5)
C14	-0.4245(9)	0.2328(7)	0.0065(5)
C15	-0.3036(9)	0.2551(6)	0.0419(4)
C16	-0.2335(8)	0.2094(6)	0.1008(4)
C21	-0.2798(7)	-0.0169(5)	0.1931(4)
C22	-0.3737(7)	-0.0245(6)	0.2157(4)
C23	-0.4377(7)	-0.1044(6)	0.2056(4)
C24	-0.4097(7)	-0.1707(6)	0.1721(4)
C25	-0.3184(7)	-0.1610(5)	0.1495(4)
C26	-0.2503(7)	-0.0844(6)	0.1594(4)
C31	-0.2246(7)	0.1457(6)	0.2666(4)
C32	-0.2049(7)	0.1063(6)	0.3275(4)
C33	-0.2178(7)	0.1575(7)	0.3781(4)
C34	-0.2454(8)	0.2467(7)	0.3673(5)
C35	-0.2626(8)	0.2832(7)	0.3082(5)
C36	-0.2545(7)	0.2337(6)	0.2571(4)
C41	0.0515(7)	-0.0356(5)	0.3574(4)
C42	0.0479(7)	-0.0406(6)	0.4204(4)
C43	-0.0085(8)	-0.1104(7)	0.4362(4)
C44	-0.0599(8)	-0.1766(7)	0.3888(5)
C45	-0.0582(8)	-0.1714(6)	0.3254(4)
C46	-0.0022(7)	-0.1017(6)	0.3098(4)
C51	0.1397(6)	0.1422(5)	0.3883(4)
C52	0.2278(8)	0.1363(6)	0.4521(4)
C53	0.2382(8)	0.2028(7)	0.4984(4)
C54	0.1613(8)	0.2745(6)	0.4789(4)
C55	0.0765(7)	0.2815(6)	0.4153(5)
C56	0.0614(7)	0.2168(6)	0.3672(4)
C61	0.2780(6)	0.0232(5)	0.3476(4)
C62	0.3170(8)	-0.0625(6)	0.3612(5)
C63	0.4409(8)	-0.0795(7)	0.3740(6)
C64	0.5239(7)	-0.0214(7)	0.3751(5)
C65	0.4836(7)	0.0621(7)	0.3597(5)
C66	0.3618(7)	0.0846(6)	0.3460(4)

21.580(5) Å, β 112.98(2)°, space group $P2_1/c$. At room temperature, 9236 reflections were measured, of which 8495 were unique. Intensities of reflections were corrected for Lorentz and polarization factors. No absorption correction was applied. After averaging equivalent reflections 2590 reflections with $I \geq 3\sigma(I)$ 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 positions of the Ni atom and the two P atoms. The remaining atoms were located in subsequent difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined anisotropically for all non-hydrogen atoms by least-squares techniques to $R = 0.058$ ($R_w = 0.065$). The highest peak in the final difference Fourier had a height of 1.09 e Å⁻³. The final atomic parameters are listed in Table 2. Tables of atomic coordinates of H atoms, anisotropic thermal parameters for other atoms and interatomic distances and bond angles 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 the title compound is shown in Fig. 1 together with the numbering scheme. Figure 2 depicts a stereo plot of the molecule, and 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 nickel atom is trigonal-planar coordinated. The dihedral angle between the normals to the planes through P1, Ni, P2 and C1, Ni, C2 is 9.7(5)°. The Ni–P bond lengths are 2.184(2) and 2.182(2) Å. The P1NiP2 angle is 109.50(8)°. The average values of the phosphorus–carbon and the carbon–carbon bond lengths in the phenyl rings are 1.852(6) and 1.383(9) Å respectively. These bond lengths are typical for the triphenylphosphane nickel moiety [9], but the carbon–carbon bond lengths in the

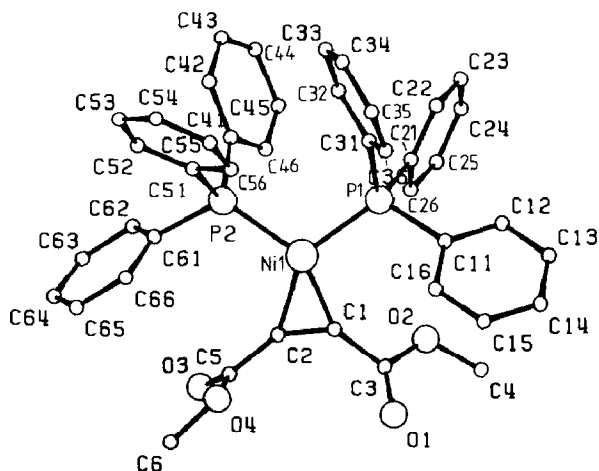


Fig. 1. The (η^2 -acetylenedimethyldicarboxylate)bistriphenylphosphane)nickel(0) molecule (I) with numbering scheme.

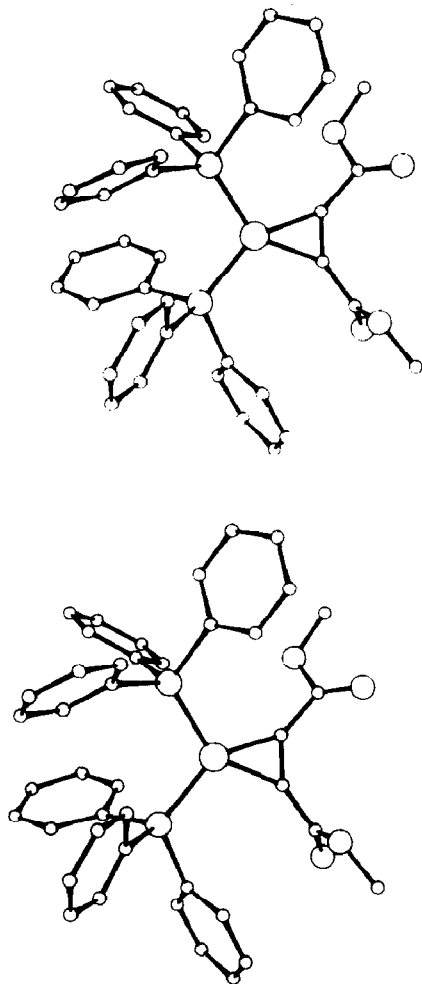


Fig. 2. Stereo plot of I.

phenyl rings vary from 1.32(2) to 1.432(9) Å, the large deviations from the standard value of 1.39 Å [11] being due to the intense thermal motion of the C14, C24, C34, C44, C54, C64 atoms and their neighbouring carbons. Both triphenylphosphane ligands have a propeller conformation, which corresponds to minimal steric hindrance. The alkyne ligand is coordinated “side-on” at the carbon–carbon triple bond. The nickel–alkyne C atom distances differ slightly: 1.848(6) and 1.878(7) Å. The C1NiC2 angle is 40.1(2)°. The coordinated alkyne is no longer linear but displays *cis* geometry. The deviation from linearity (the bond angles C1C2C5 and C2C1C3 are 144.7(7)° and 137.9(6)°, respectively) is characteristic of η -coordinated alkynes [10]. The C1–C2 distance of 1.279(8) Å lies between those for normal C≡C (1.20 Å) and C=C bonds (1.34 Å).

Influence of metals

It is evident from Table 4 that the bond length of the coordinated acetylenic triple bond is almost identical with that for the nickel(0) and palladium(0) com-

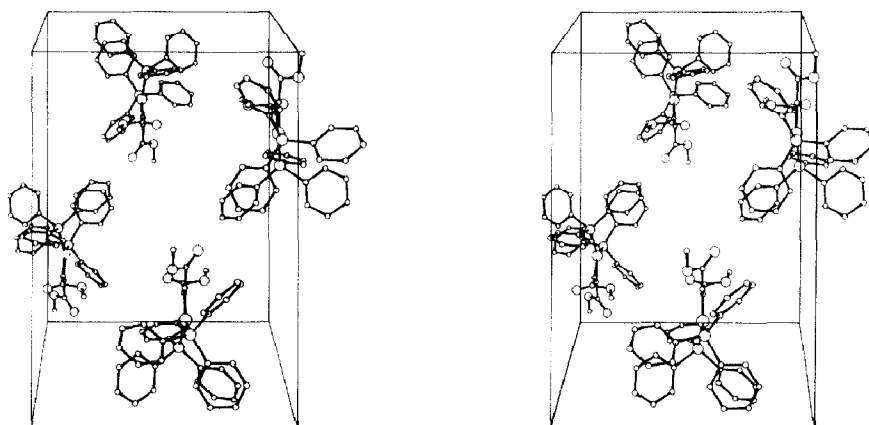


Fig. 3. Molecular packing in the crystal of I.

plexes. But the nature of the metal is important, because noticeably shorter M–C bond lengths of 1.848(2) and 1.878(7) Å are observed in the nickel complex $(\text{Ph}_3\text{P})_2\text{Ni}(\text{MeOCC}_2\text{COOMe})$ compared with 2.051(6) and 2.047(6) Å in the palladium analog $(\text{Ph}_3\text{P})_2\text{Pd}(\text{MeOCC}_2\text{COOMe})$ [7].

Table 3

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

Ni–P1	2.184(2)	P1–Ni–P2	109.50(8)
Ni–P2	2.182(2)	P1–Ni–C1	103.6(3)
Ni–C1	1.848(6)	P1–Ni–C2	143.5(2)
Ni–C2	1.878(7)	P2–Ni–C1	146.1(3)
P1–C11	1.862(7)	P2–Ni–C2	106.9(2)
P1–C21	1.853(6)	C1–Ni–C2	40.1(2)
P1–C31	1.854(7)	Ni–P1–C11	113.9(2)
P2–C41	1.848(6)	Ni–P1–C21	117.7(2)
P2–C51	1.844(6)	C11–P1–C21	101.4(4)
P2–C61	1.853(6)	C11–P1–C31	103.4(3)
O1–C3	1.198(8)	C21–P1–C31	103.3(3)
O2–C3	1.345(8)	Ni–P2–C41	110.1(2)
O2–C4	1.446(8)	Ni–P2–C51	122.7(3)
O3–C5	1.215(8)	Ni–P2–C61	115.8(2)
O4–C5	1.36(1)	C3–O2–C4	116.9(6)
O4–C6	1.439(8)	C5–O4–C6	117.5(7)
C1–C2	1.279(8)	Ni–C1–C2	71.2(4)
C1–C3	1.440(9)	Ni–C1–C3	150.8(5)
C2–C5	1.428(9)	C2–C1–C3	137.9(6)
		Ni–C2–C1	68.6(5)
		Ni–C2–C5	146.6(5)
		C1–C2–C5	144.7(7)
		O1–C3–O2	122.1(8)
		O1–C3–C1	126.9(8)
		O2–C3–C1	110.8(7)
		O3–C5–O4	120.7(6)
		O3–C5–C2	110.9(8)

Table 4

Spectroscopic and geometric parameters of $(\text{Ph}_3\text{P})\text{M}(\text{MeOOC}_2\text{COOMe})$ ($\text{M} = \text{Ni}, \text{Pd}$)

M:	Ni	Pd
$\Delta\nu(\text{C}\equiv\text{C})$ (cm^{-1})	449	411–26 [7]
Distances (\AA)		
C–C	1.279(8)	1.279(11)
M–C	1.848(2)	2.051(6)
	1.878(7)	2.074(6)
M–P	2.184(2)	2.330(2)
	2.182(2)	2.321(2)
Angles ($^\circ$)		
C–C–COOMe	144.7(7)	146.4(7)
	137.9(6)	144.9(7)
bend-back	35.3(7)	33.6(7)
	42.1(6)	35.1(7)
C–M–C	40.1(2)	36.1(3)
P–M–P	109.51	107.43(6)
dihedral, PMP/CMC	9.7(5)	9.7(4)

This effect is not observed in $(\text{Cy}_3\text{P})_2\text{M}(\text{F}_3\text{CC}_2\text{CF}_3)$ with $\text{M} = \text{Pd}$ and Pt [8] (Table 5) where the M–C bond distances and the mean bend-back angles are almost identical. Thus the smaller difference in atomic radii of Pd and Pt and to some extent the increased steric bulk of Cy_3P in the latter complexes may have caused the changes. The same tendency is obviously displayed in the C–M–C angles, which are significantly different in the Ph_3P complexes of nickel(0) and palladium(0) but nearly identical in the Cy_3P complexes of platinum(0) and palladium(0). Thus in the case of alkyne complexes of similar metals the effects of alkyne substituents or

Table 5

Spectroscopic and geometric parameters [8] of $(\text{Cy}_3\text{P})_2\text{M}(\text{F}_3\text{CC}_2\text{CF}_3)$ ($\text{M} = \text{Pd}, \text{Pt}$)

M:	Pt	Pd
$\Delta\nu(\text{C}\equiv\text{C})$ (cm^{-1})	570	538
Distances (\AA)		
C–C	1.260(10)	1.271(10)
M–C	2.047(7)	2.040(8)
	2.045(8)	2.053(8)
M–P	2.309(2)	2.358(2)
	2.301(2)	2.363(2)
Angles ($^\circ$)		
C–C– CF_3	133.7(8)	137.1(9)
	135.4(8)	135.0(8)
bend-back	46.3(8)	42.9(9)
	44.6(8)	45.0(8)
C–M–C	35.9(3)	36.2(3)
P–M–P	110.23(6)	111.01(7)
dihedral, PMP/CMC	6.5(5)	2.8(4)

other ligands on the structure seems to be more important than the nature of the metal atom.

References

- 1 A.C. Hopkinson in, S. Patai (Ed.), "The Chemistry of the Carbon Carbon Triple Bond", John Wiley & Sons, Chichester–New York–Brisbane–Toronto, 1978, p. 75.
- 2 E.O. Greaves, C.J.L. Lock, P. Maitlis; *Can. J. Chem.* 46 (1968) 3879.
- 3 U. Rosenthal, *Z. Anorg. Allg. Chem.* 482 (1981) 179.
- 4 U. Rosenthal, *Z. Anorg. Allg. Chem.* 513 (1984) 151.
- 5 S. Otsuka, A. Nakamura, *Adv. Organomet. Chem.* 14 (1976) 245.
- 6 U. Rosenthal, H. Görls, *J. Organomet. Chem.* 348 (1988) 135.
- 7 J.A. McGinney, *J. Chem. Soc., Dalton Trans.* (1974) 1038.
- 8 D.H. Farrar, N.C. Payne, *J. Organomet. Chem.* 220 (1981) 251.
- 9 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.
- 10 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, *Disertation, Bochum* (1983). U. Rosenthal, W. Schulz, H. Görls, *Z. Anorg. Allg. Chem.* 550 (1987) 169.
- 11 M.G. Brown, *Trans. Faraday Soc.* 55 (1955) 694.