ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2017, Vol. 43, No. 12, pp. 837–842. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © A.A. Pasynskii, S.S. Shapovalov, I.V. Skabitskii, O.G. Tikhonova, 2017, published in Koordinatsionnaya Khimiya, 2017, Vol. 43, No. 12, pp. 739–743.

Syntheses and Structures of Nickel–Tungsten μ-Tellurophenyl Complexes CpNi(PPh$_3$)(μ-TePh)W(CO)$_5$ and [CpNi(PPh$_3$)(μ-TePh)]$_2$W(CO)$_4$

A. A. Pasynskii*, S. S. Shapovalov, I. V. Skabitskii, and O. G. Tikhonova
Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia
**e-mail: aapasgugl@gmail.com*

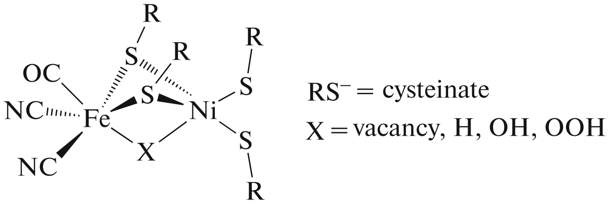
Received July 3, 2017

Abstract—Syntheses and molecular structures of the heterometallic complexes of nickel cyclopentadienyl triphenylphosphine tellurophenolate with tungsten carbonyls (**II** and **III**) (CIF files CCDC nos. 1559733 and 1559734, respectively) are described.

Keywords: cyclopentadienyl, metal carbonyls, nickel, tungsten, tellurophenyl bridges, X-ray diffraction analysis
DOI: 10.1134/S1070328417120065

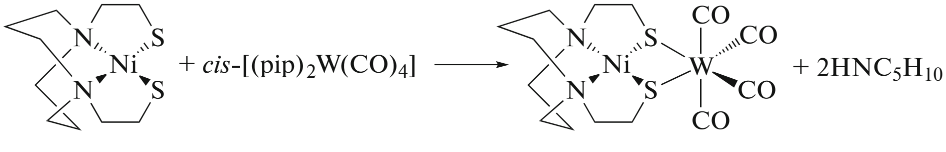
INTRODUCTION

The heterometallic clusters based on the nickel chalcogenate complexes as ligands are interesting due to modeling of enzyme active centers of the Ni–Fe hydrogenase type [1].

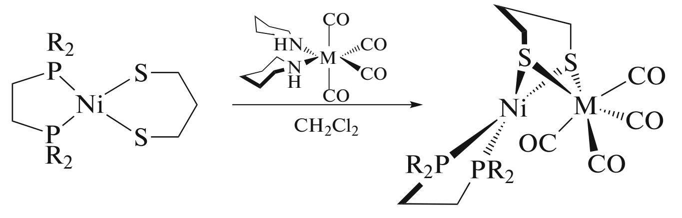


Active center of Ni–Fe hydrogenase

Several methods for the formation of these clusters are described in the literature. In this case, the S-donating nickel-containing fragments with ligands of the 1,5-(1,5-diazacyclooctane)diethylthiolate type substitute labile ligands (piperidine, tetrahydrofuran (THF), acetonitrile) in the tungsten complexes [2].



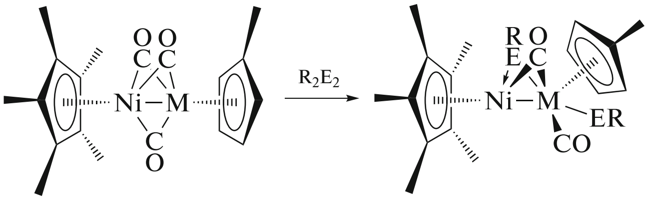
The molybdenum and tungsten carbonyl complexes react similarly with the nickel complex having chelate phosphine ligands Dppe or Dcpe in combination with the dianionic sulfur ligand Pdt^{2-} (–S(CH$_2$)$_3$S–) [3].



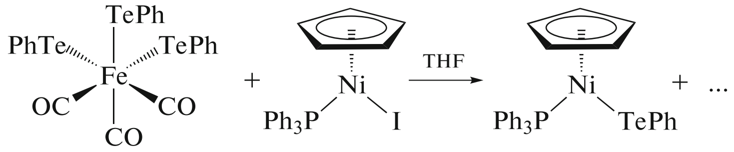
M = Mo, W R = Ph, Cy

In these clusters, according to the X-ray diffraction data, nickel exists in the square environment, whereas the environment of molybdenum or tungsten is octahedral. The Ni–M bond is absent (in all cases, the distance between nickel and the metal in the NiS_2M core is longer than the sum of covalent radii of these metals (Ni 1.24, Mo 1.54, W 1.62 Å) [4]).

The unsaturated complexes $[(\eta\text{-}C_5Me_5)Ni\text{–}M(CO)_3(\eta\text{-}C_5H_4Me)]$ (M = W or Mo) react with diphenyl disulfide, dimethyl disulfide, or diphenyl diselenide via oxidative addition at the Ni–M bond to form complexes of the general formula $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)(\mu\text{-}ER)M(CO)(ER)(\eta\text{-}C_5H_4Me)$. In particular, at ER = SPh and M = W, according to the X-ray diffraction data, one bridging and one terminal thiophenolate ligands, as well as the Ni–W bond 2.602 Å long, are observed (the Ni–S (2.160 Å) and W–S (2.503 Å) bonds are substantially shortened) [5].



We were interested in the nickel tellurophenolate complex, $CpNi(PPh_3)(TePh)$ (**I**), synthesized by the Chinese chemists using the reaction of $CpNi(PPh_3)I$ with *fac*-$[Fe(CO)_3(TePh)_3]^-$ [6], which acts as a source of phenyltelluride anions.



We have previously shown that the $Me_4C_4Co(CO)_2(TePh)$ complex isoelectronic to complex **I** can react with $(THF)W(CO)_5$ to give the heterometallic complex $Me_4C_4Co(CO)_2(\mu\text{-}TePh)W(CO)_5$ [7]. In this work, we used a simpler method for the synthesis of complex **I** and studied its reactions with the tungsten carbonyl complexes.

EXPERIMENTAL

All reactions and procedures on the isolation of the reaction products were carried out under an argon atmosphere and in absolute solvents. The temperature of the photochemical process was maintained constant using a Huber CC 805 thermostat with a Pilot ONE attachment. A high-pressure mercury lamp (400 W) was used for UV irradiation. IR spectra were recorded on a Bruker Alpha spectrophotometer in KBr pellets and in CaF_2 cells. Thin layer chromatography (TLC) was conducted on the plates of silica 60 F_{254} on the aluminum support (Merck). The reactant $CpNi(PPh_3)Cl$ was obtained using a described procedure [8].

Synthesis of $CpNi(PPh_3)(TePh)$ (I). A suspension of metallic Na excess in THF (50 mL) was added to Te_2Ph_2 (1.088 g, 2.653 mmol) with continuous stirring. The starting orange-vinous solution almost decolorized in 25 min. The resulting solution was added to $CpNi(PPh_3)Cl$ (2.24 g, 5.314 mmol). A dark vinous solution was formed and evaporated to dryness in a water-jet pump vacuum. The dark brown precipitate was washed with heptane (30 mL), and the organics was extracted with benzene (100 mL). The obtained brown solution was concentrated to 1/3 of the volume, and heptane (30 mL) was added. The solution was concentrated and kept at 0°C. The precipitated brown crystals of complex **I** were dried in vacuo. The yield was 0.65 g (59%).

TLC: benzene–heptane (1 : 1), $R_f = 0.36$, pink spot.

IR (KBr), ν, cm^{-1}: 3043 w, 2924 w, 2022 vw, 1943 vw, 1735 vw, 1701 vw, 1685 vw, 1569 m, 1478 m, 1468 m, 1432 s, 1430 vw, 1384 w, 1384 w, 1308 vw, 1182 vw, 1159 vw, 1109 vw, 1096 s, 1060 vw, 1047 vw, 1028 vw, 1014 m, 995 w, 900 vw, 834 m, 791 s, 688 vw, 651 vw, 618 s, 533 s, 510 s, 492 s, 458 vw, 451 m, 421 m.

^{31}P NMR for **I** (δ, ppm): 62.4, $^2J_{\text{Te–P}} = 165$ Hz. ^{125}Te NMR (δ, ppm): –183.0, $^2J_{\text{Te–P}} = 165$ Hz.

Synthesis of CpNi(PPh$_3$)(μ-TePh)W(CO)$_5$ (II). A solution of W(CO)$_6$ (0.306 g, 0.870 mmol) in THF (40 mL) was cooled to –70°C and UV-irradiated with argon bubbling. In 1 h, a yellow solution was formed and added to complex **I** (0.514 g, 0.870 mmol). The solution was dried to dryness, and the residue was washed with pentane (20 mL) and then dissolved in toluene (20 mL). The filtered solution was evaporated to half a volume, heptane (5 mL) was added to the onset of crystallization, and the mixture was kept in a refrigerator. The precipitated crimson crystals were separated and dried with a water-jet pump. The yield was 0.45 g (56%).

TLC: benzene–heptane (3 : 1), $R_f = 0.43$, crimson spot.

IR (KBr), ν, cm^{-1}: 3057 br.vw, 2923 br.vw, 2852 br.vw, 2057 s, 1977 s, 1969 s, 1927 s, 1907 vs, 1897 s, 1587 vw, 1571 vw, 1478 vw, 1471 vw, 1433 w, 1400 vw, 1384 vw, 1347 vw, 1261 vw, 1160 vw, 1097 w, 1015 vw, 988 vw, 834 vw, 788 w, 747 w, 740 w, 692 m, 650 vw, 597 m, 577 m, 533 m, 509 w, 491 vw, 456 w, 430 w.

Synthesis of a mixture of CpNi(PPh$_3$)(μ-TePh)-W(CO)$_5$ (II) and [CpNi(PPh$_3$)(μ-TePh)]$_2$W(CO)$_4$ (III). A weighed sample of W(CO)$_6$ (0.082 g, 0.23 mmol) was dissolved in THF (20 mL). The colorless solution was UV-irradiated at room temperature for 1 h to obtain a yellow solution, which was filtered to complex **I** (0.14 g, 0.24 mmol). The solution turned brown and was evaporated to dryness in a water-jet pump vacuum. The residue was washed with heptane and dissolved in CH$_2$Cl$_2$ (20 mL). A crimson solution was formed, which was repeatedly filtered and concentrated until the crystallization of the product. The mother liquor was kept for 1.5 h at –18°C. The formed crystals were separated and washed with heptane. The yield of complex **II** was 0.040 g (19%).

The mother liquor was additionally kept at –18 °C for 12 h. The formed crimson crystals were recrystallized from a benzene–heptane mixture. Several crystals of compound **III** suitable for X-ray diffraction analysis were obtained.

X-ray diffraction analyses were carried out on a Bruker APEX II CCD diffractometer. An absorption correction was applied by the method of multiple equivalent reflection measurements using the SADABS program [9]. The structures of compounds **II** and **III** were determined by a direct method and refined by least squares for F^2 in the anisotropic approximation of non-hydrogen atoms using the SHELX-2014 [10] and OLEX2 [11] program packages. The coordinates of the disordered atoms of the cyclopentadienyl ligand in complex **II** were refined in the isotropic approximation with a constraint of equal distances (SAME and SADI instructions). The positions of the hydrogen atoms were calculated geometrically. The crystallographic data and refinement parameters for the structures of compounds **II** and **III** are presented in Table 1. Selected bond lengths and bond angles in compounds **II** and **III** are given in captions to Figs. 1 and 2.

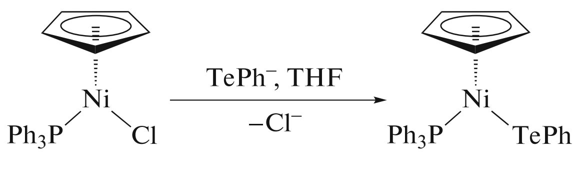
The coordinates of atoms and other parameters for the structures of compounds **II** and **III** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1559733 and 1559734, respectively; http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Heterometallic complex **II** was synthesized via the following scheme.

$$\mathrm{Cp_2Ni} \xrightarrow{\mathrm{CCl_4/PPh_3}} \mathrm{CpNi(PPh_3)Cl} \xrightarrow{\mathrm{PhTeNa}} \mathrm{CpNi(PPh_3)TePh} \xrightarrow{\mathrm{W(CO)_5THF}} \mathrm{CpNi(PPh_3)TePhW(CO)_5}^{\mathrm{S}}$$

The starting semisandwich 18-electron complex CpNi(PPh$_3$)Cl (**IV**) was synthesized from 20-electron sandwich nickelocene using a known procedure [8]. When compound **IV** reacts with the phenyltelluride anion (the product of the reduction of diphenylditellurium with sodium), the chlorine atom is replaced by phenyl telluride to form compound **I**.



The individual character of the obtained compound **I** was confirmed by the TLC data, and its identity was proved by a comparison of the spectrum of the synthesized substance with that of authentic compound **I** [6].

Tungsten hexacarbonyl in THF at –70°C undergoes a photochemical transformation to form W(CO)$_5$(THF) in which **I** readily substitutes a THF molecule to form a new heterometallic complex **II**. The TLC of the reaction product in a benzene–heptane (3 : 1) system gives only one crimson spot, indicating that the compound is individual. The IR spectrum of compound **II** contains CO absorption bands at 2057, 1977, 1969, 1927, 1907, and 1897 cm^{-1} corresponding to those observed for the W(CO)$_5$ fragment in the spectrum of the isoelectronic complex Me$_4$C$_4$Co(CO)$_2$(μ-TePh)W(CO)$_5$ [7].

The structure of complex **II** was established by X-ray diffraction analysis (Fig. 1, Table 1).

Table 1. Crystallographic data and the structure refinement parameters for complexes **II** and **III**

Parameter	Value	
	II	**III**
Empirical formula	$C_{34}H_{25}O_5PNiTeW$	$C_{63}H_{52}O_4Cl_2P_2 Ni_2Te_2W$
FW	914.67	1562.35
Radiation (λ, Å)	MoK_α (λ = 0.71073)	
Temperature, K	150(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a, Å	42.301(2)	19.827(2)
b, Å	9.5043(5)	12.4538(9)
c, Å	32.162(2)	23.348(2)
β, deg	99.2004(9)	97.147(1)
V, Å^3	12764(1)	5720.3(7)
Z	16	4
ρ_{calcd}, g cm^{-3}	1.904	1.814
μ, mm^{-1}	5.178	3.855
F(000)	7008.0	3040.0
Scan θ range, deg	1.95–61.066	4.14–58.344
Scan mode	ω	
Independent reflections (N_1)	19515 (R_{int} = 0.0422)	7691 (R_{int} = 0.0628)
Reflections with $I > 2\sigma(I)$ (N_2)	15187	5211
Number of refined parameters	771	349
Goodness-of-fit (F^2)	1.010	1.049
R_1 for N_2	0.0298	0.0564
wR_2 for N_1	0.0636	0.1665
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	0.98/–0.76	2.85/–1.36

The both M–Te bonds (Ni–Te 2.4926(5), W–Te 2.8519(3) Å) turned out to be noticeably shortened compared to the sum of covalent radii ($r_{Ni} + r_{Te} = 2.62$, $r_W + r_{Te} = 3.00$ Å) [4], which indicates their partial multiplicity, probably, due to the additional dative interaction of unpaired electron pairs of the metal with the vacant orbitals of the tellurium atom. The Ni–P bond (2.152(1) Å) is shortened compared to the sum of covalent radii ($r_{Ni} + r_P = 2.31$ Å) for the same reason [4].

The formation of minor amounts of tungsten–dinickel complex **III** is probably due to the formation of the $W(CO)_4(THF)_2$ complex under UV irradiation

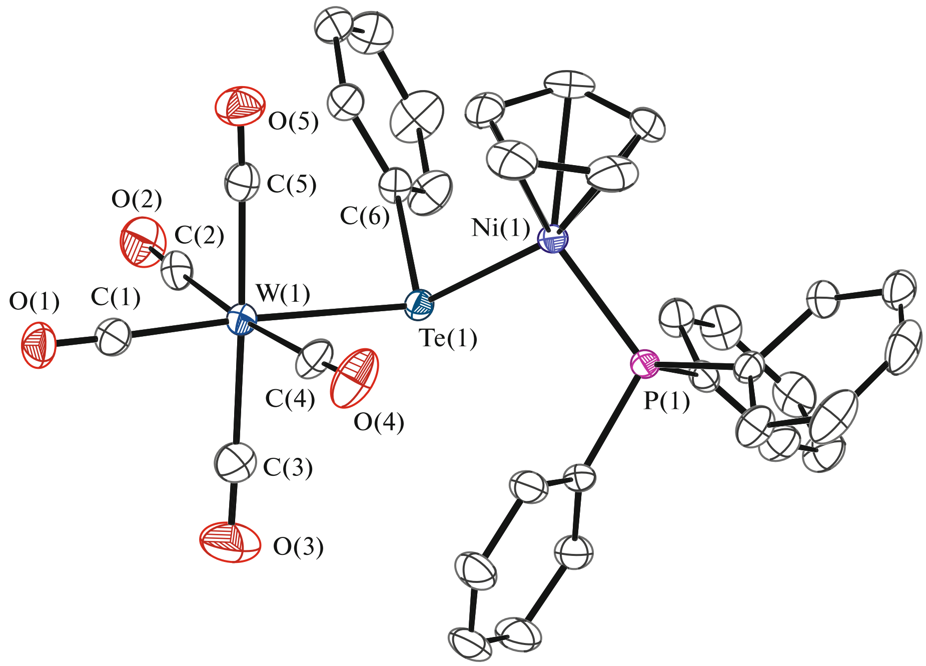


Fig. 1. Molecular structure of $CpNi(PPh_3)(\mu\text{-}TePh)W(CO)_5$ (**II**). One of two independent molecules is shown. Selected bond lengths and angles: W(1)–Te(1) 2.8442(3), Te(1)–Ni(1) 2.4912(5), Ni(1)–P(1) 2.1432(10), W(2)–Te(2) 2.8519(3), Te(2)–Ni(2) 2.4926(5), and Ni(2)–P(2) 2.152(1) Å and Ni(2)Te(2)W(2) 111.174(14)°, Ni(1)Te(1)W(1) 109.412(14)°.

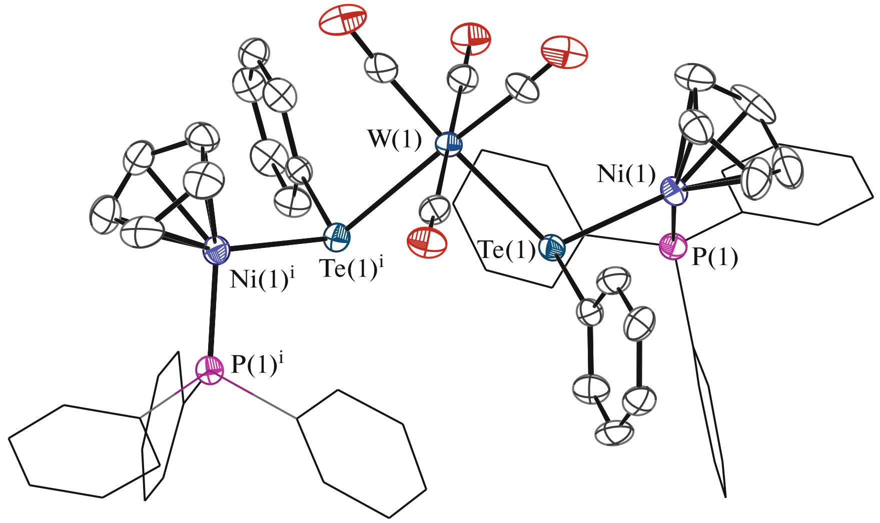


Fig. 2. Molecular structure of $[CpFe(CO)(PPh_3)(\mu\text{-}TePh)]_2W(CO)_4$ (**III**) (the phenyl groups of the triphenylphosphine ligands are shown by lines for clarity). Selected bond lengths and angles: Te(1)–Ni(1) 2.507(1), Te(1)–W(1) 2.8645(9), and Ni(1)–P(1) 2.150(2) Å and Ni(1)Te(1)W(1) 115.11(3)°.

at room temperature. Unfortunately, spectral characteristics were not obtained because of a small amount of the substance. As in the case of complex **II**, a substantial shortening of the Te–Ni (2.507(1) Å), Te–W (2.8645(9) Å), and Ni–P (2.150(2) Å) bonds is observed, and the complex has the *cis* structure with the TeWTe (83.93(3)°) and NiTeW (115.11(3)°) angles (Fig. 2).

Thus, it is shown that nickel complex **I**, as the earlier studied compounds $Me_4C_4Co(CO)_2(TePh)$ [7] and $CpFe(CO)(PPh_3)TePh$ [12], is capable of coordinating to tungsten carbonyls through the μ-tellurophenyl bridge, and all bonds of transition metals with tellurium are strongly shortened compared to the sums of covalent radii.

ACKNOWLEDGMENTS

This work was supported by the Federal Agency of Scientific Organizations and the Russian Foundation for Basic Research (project no. 16-03-00798).

REFERENCES

1. De Lacey, A.L., Fernandez, V.M., Rousset, M., and Cammack, R., *Chem. Rev.*, 2007, vol. 107, p. 4304.
2. Rampersad, M.V., Jeffery, S.P., Reibenspies, J.H., et al., *Angew. Chem., Int. Ed. Engl.*, 2005, vol. 44, p. 1217.
3. Schilter, D., Fuller, A.L., and Gray, D.L., *Eur. J. Inorg. Chem.*, 2015, vol. 2015, p. 4638.
4. Cordero, B., Gómez, V., Platero-Prats, A.E., et al., *Dalton Trans.*, 2008, p. 2832.
5. Bartlone, A.F., Chetcuti, M.J., Fanwick, P.E., and Haller, K.J., *Inorg. Chem.*, 1993, vol. 32, p. 1435.
6. Hsich, C.-K., Lo, F.-C. Lee, G.-H., et al., *J. Chinese Chem. Soc.*, 2000, vol. 47, p. 103.
7. Pasynskii, A.A., Skabitsky, I.V., Shapovalov, S.S., et al., *Russ. Chem. Bull.*, 2007, vol. 56, no. 9, p. 1731.
8. Ustynyuk, Yu.A., Voevodskaya, T.I., Zharikova, N.A., and Ustynyuk, N.A., *Dokl. Akad. Nauk SSSR*, 1968, vol. 181, no. 2, p. 372.
9. SADABS (version 2008/1), Madison: Bruker AXS Inc., 2008.
10. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
11. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339.
12. Pasynskii, A.A., Shapovalov, S.S., Tikhonova, O.G., et al., *Russ. J. Coord. Chem.*, 2015, vol. 41, no. 11, p. 741.

Translated by E. Yablonskaya