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# Chalcogenide Complexes of Cyclopentadienylnickel with Heterocyclic Carbene

**S. S. Shapovalov**[a, *], **A. A. Pasynskii**[a], **I. V. Skabitskii**[a], **O. G. Tikhonova**[a], **A. V. Kolos**[a], and **M. O. Grigor'eva**[a]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*

**e-mail: schss@yandex.ru*

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**Abstract**—The monomeric complex $(\eta^5\text{-}C_5H_5)Ni(Me_2Im)S^nPr$ synthesized by the reaction of the $[(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}S^nPr)]_2$ dimer with dimethylimidazolium carboxylate is rapidly oxidized in air to form the sulfone complex $(\eta^5\text{-}C_5H_5)Ni(Me_2Im)S(O)_2{}^nPr$ (**I**), while its reaction with the adduct $W(CO)_5(THF)$ affords $(\eta^5\text{-}C_5H_5)Ni(Me_2Im)(\mu\text{-}S^nPr)W(CO)_5$ (**II**). A new heterometallic complex $(\eta^5\text{-}C_5H_5)Ni(Me_2Im)TeI_2Fc$ (**III**) containing the terminal telluroferrocenyl fragment is obtained by the reaction of the known nickel carbene complex $(\eta^5\text{-}C_5H_5)Ni(Me_2Im)I$ with FcTeI (Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$). The complexes synthesized are studied by X-ray structure analysis (CIF files CCDC nos. 1835574, 1835573, and 1835572 for compounds **I**, **II**, and **III**, respectively).

*Keywords:* nickel, carbene, chalcogen, N-heterocyclic carbenes, X-ray structure analysis

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## INTRODUCTION

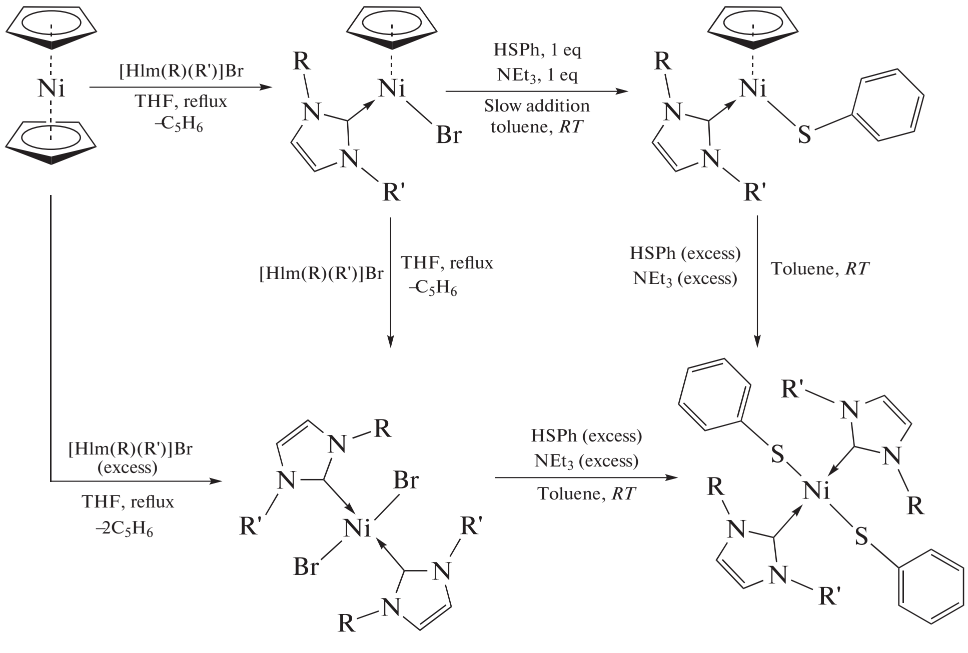
In N-heterocyclic carbenes, the carbene carbon atom is bound to two nitrogen atoms stabilizing carbene due to the interaction of the vacant orbital of carbon and electron pairs of the nitrogen atoms. Heterocyclic carbenes are strong σ-donors and weak π-acceptors, which enables one to use them as stabilizing ligands in the chemistry of organoelement compounds [1]. When studying the chemistry of N-heterocyclic carbene complexes with transition metals, special attention is given to the nickel(II) complexes because of their catalytic activity in a number of organic reactions [2] (for example, in the Suzuki and Kumada cross-coupling reactions and in the polymerization of styrene and nonbornene).

The C–H activation of imidazolium salts (Scheme 1) is used for the synthesis of the nickel cyclopentadienyl complexes with N-heterocyclic carbene ligands [3]. For example, the reactions of nickelocene [4] or bis(indenyl)nickel and imidazolium halide salts afford derivatives of the $(\eta^5\text{-}C_5H_5)Ni(NHC)(X)$ (X = Cl, Br, I) type, which, in turn, can be transformed into the thiolate derivatives using the substitution of the coordinated halogen atom by mercaptane in the presence of triethylamine. In this case, the thiolate nickel complexes $(NHC)_2Ni(SR)_2$ are formed in a mercaptane excess [5].

However, a more convenient method for the synthesis of carbene complexes is the use of 1,3-bis(methyl)imidazolium carboxylate as a precursor due to its resistance to air and the capability of reacting with a number of organoelement compounds [6]. The use of dimethylimidazolium carboxylate provides wide possibilities for the development of the chemistry of chalcogenide complexes based on cyclopentadienylnickel(II). These compounds make it possible to obtain the heterometallic derivatives in the reactions where the aforementioned chalcogenide complexes act as bridging ligands between various metal fragments.

## EXPERIMENTAL

All reactions and manipulations on the isolation of products were carried out under argon in anhydrous solvents. The photochemical process was temperature-controlled on a Huber CC 805 thermostat with a Pilot ONE attachment. A high-pressure (400 W) mercury lamp was used for UV irradiation. IR spectra were recorded on a Bruker Alpha spectrophotometer with a Platinum ATR attachment for attenuated total reflection (ATR). An EA3000 CHNS analyzer (EuroVector) was used for chemical analysis. Diferrocenylditellurium [7], $(\eta^5\text{-}C_5H_5)Ni(Me_2Im)I$ [8], $((\eta^5\text{-}C_5H_5)\text{-}NiS^nPr)_2$ [9], and dimethylimidazolium carboxylate [6] were obtained according to published procedures.



R = MePh, R' = MePh/EtPh;

R = Me/MePh, R' = 4-$NO_2$(MePh)

**Scheme 1.**

**Synthesis of ($\eta^5$-$C_5H_5$)Ni($Me_2$Im)S(O)$_2$$^n$Pr (I).** Dimethylimidazolium carboxylate (0.26 g, 1.9 mmol) was added to [($\eta^5$-$C_5H_5$)Ni($\mu$-S$^n$Pr)$_2$] (0.3 g, 0.76 mmol) in a mixture of toluene (10 mL) and acetonitrile (10 mL), and the resulting mixture was refluxed for 2 h. The color of the solution changed to yellow-brown. The solvent was removed in vacuo, and the residue was extracted with dichloromethane. The extract was concentrated to 3 mL and crystallized with pentane by the method of diffusion through the gas phase. The yield of yellow-brown prismatic crystals was 0.11 g (45%).

For $C_{13}H_{20}N_2O_2SNi$ (*FW* = 327)

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 47.74 | H, 6.16 | N, 8.56 |
| Found, % | C, 47.38 | H, 5.41 | N, 8.63 |

IR (ATR), ν, cm$^{-1}$: 3148 w, 3093 m.br, 2958 w, 2928 m.br, 2869 w, 1671 w, 1569 w, 1461 s.br, 1397 s, 1377 m, 1349 w, 1280 w, 1232 s, 1157 vs, 1082 m, 1019 vs.br, 893 w, 835 m, 788 s.br, 751 s, 739 vs.br, 701 vs.br, 681 s, 639 m, 593 vs, 531 m, 494 m, 471 m, 444 w, 408 w.

**Synthesis of ($\eta^5$-$C_5H_5$)Ni($Me_2$Im)($\mu$-S$^n$Pr)W(CO)$_5$ (II).** A solution of W(CO)$_5$(THF), which was obtained by the UV irradiation of W(CO)$_6$ (0.11 g, 0.31 mmol) in THF (20 mL) for 45 min with argon bubbling, was added to the freshly isolated ($\eta^5$-$C_5H_5$)Ni($Me_2$Im)S$^n$Pr (0.095 g, 0.31 mmol). The mixture was magnetically stirred for 20 min, and then the solvent was removed in vacuo. The same compound is formed upon the extraction with pentane or benzene followed by recrystallization from a dichloromethane–hexane mixture and crystallizes from a dichloromethane–pentane mixture as orange prisms suitable for X-ray structure analysis. The yield was 0.043 g (22%).

For $C_{18}H_{20}N_2O_5SNiW$ (*FM* = 619)

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 34.93 | H, 3.26 | N, 4.53 |
| Found, % | C, 35.58 | H, 3.12 | N, 4.27 |

IR (ATR), ν, cm$^{-1}$: 3139 vw.br, 2959 vw.br, 2917 vw, 2870 vw, 2058 vw, 1965 vw, 1895 vs.br, 1873 s, 1541 vw.br, 1460 vw, 1400 vw, 1352 vw, 1225 vw, 1129 vw, 1081 vw, 1018 vw.br, 942 vw, 904 vw, 835 vw, 788 vw, 744 vw, 722 vw, 677 vw, 598 vw, 583 vw, 417 vw.

**Synthesis of ($\eta^5$-$C_5H_5$)Ni($Me_2$Im)Te$I_2$Fc (III).** Diiodine (0.036 g, 0.14 mmol) and $Fc_2Te_2$ (0.089 g, 0.14 mmol) were dissolved in benzene (10 mL) to form a black-red solution. The obtained solution was added by ($\eta^5$-$C_5H_5$)Ni($Me_2$Im)I (0.10 g, 0.30 mmol), and the mixture was magnetically stirred. After 30 min, a dark precipitate was formed and filtered off, and the mother liquor was concentrated. The product was

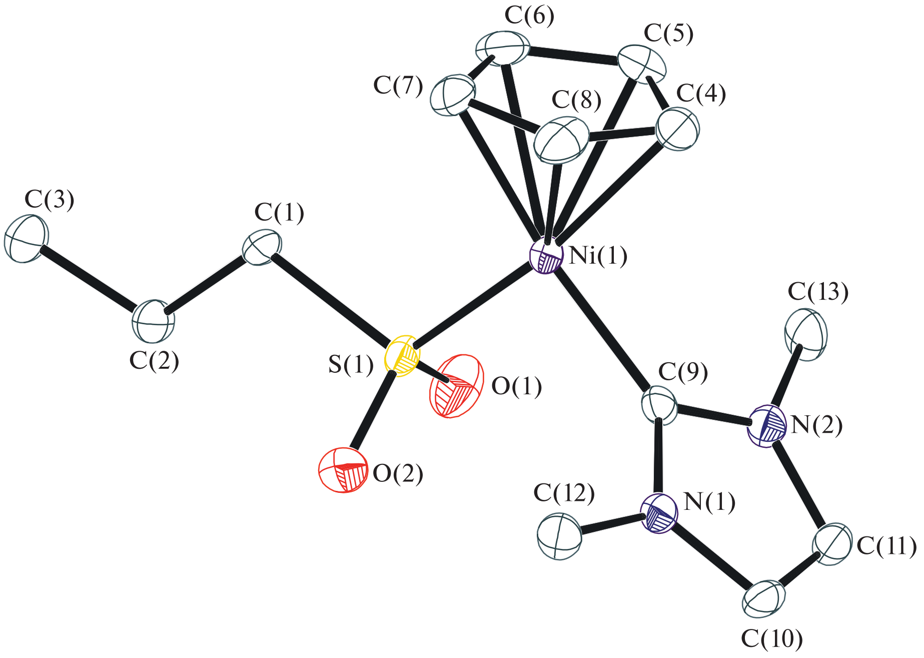


**Fig. 1.** Molecular structure of complex **I**. Selected bond lengths and angles: Ni(1)–S(1) 2.1319(5), Ni(1)–C(1) 1.885(2), S(1)–O(2) 1.471(2), S(1)–O(1) 1.460(2), S(1)–C(6) 1.803(2), N(2)–C(5) 1.459(2), N(2)–C(1) 1.351(2), N(2)–C(3) 1.379(2), N(1)–C(1) 1.355(2), N(1)–C(2) 1.382(2), N(1)–C(4) 1.458(2), C(2)–C(3) 1.345(3) Å and C(1)Ni(1)S(1) 89.18(5)°, O(1)S(1)O(2) 114.33(11)°. Hydrogen atoms are omitted for clarity.

recrystallized from a toluene–heptane mixture. The yield of brown crystals was 0.015 g (8%).

For $C_{20}H_{22}FeI_2N_2NiTe$ ($FW = 786$)

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 30.55 | H, 2.82 | N, 3.56 |
| Found, % | C, 29.92 | H, 2.41 | N, 3.89 |

IR (KBr), ν, cm$^{-1}$: 3092 vw, 1561 vw, 1408 vw, 1375 vw, 1163 w, 1128 vw, 1105 vw, 1082 vw, 1047 vw, 1022 vw, 1004 w, 819 vw, 795 vw, 738 w, 683 w, 617 w, 492 m, 478 m.

**X-ray structure analyses** were carried out on a Bruker APEX II CCD diffractometer. An absorption correction was applied by the method of multiple measurements of equivalent reflections using the SADABS program [10]. The structures of compounds **I–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 [11] and OLEX2 [12] program packages. The positions of hydrogen atoms were calculated geometrically. The crystallographic data and parameters for structure refinement of compounds **I**, **II**, and **III** are presented in Table 1. Selected bond lengths and bond angles are given in the captions to Figs. 1, 2, and 3, respectively.

The coordinates of atoms and other parameters for the structures of compounds **I–III** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1835574, 1835573, and 1835572; http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

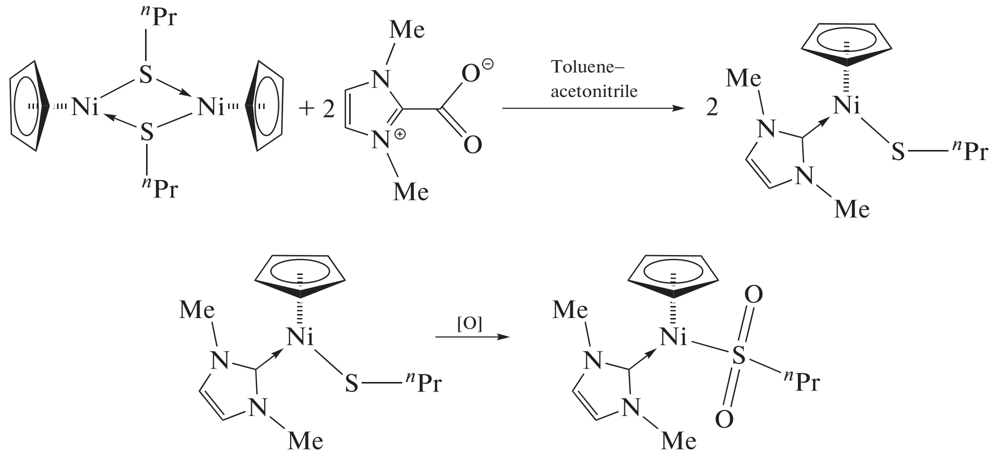
The monomeric complex ($\eta^5$-$C_5H_5$)-Ni($Me_2$Im)$S^n$Pr, obtained by the reaction of the dimer [($\eta^5$-$C_5H_5$)Ni($\mu$-$S^n$Pr)]$_2$ with dimethylimidazolium carboxylate as a yellow-brown oil, is rapidly oxidized in air to form sulfone complex **I** isolated as yellow-brown crystals (Scheme 2). The IR spectrum of complex **I** contains two bands at 1157 and 1019 cm$^{-1}$ corresponding to the ν(SO) stretching vibrations. The IR spectra of the ruthenium complexes ($\eta^5$-$C_5H_5$)Ru(Dppm)(S(O)$_2$Et) [13] with one sulfone group and the *cis*-disulfone[1,5-bis(2-mercaptoethyl)-1,5-diazocyclooctanato]nickel(II) complex [14] with two sulfone groups exhibit absorption bands at 1144, 1024 and 1032, 1071, 1180, 1192 cm$^{-1}$, respectively, characteristic of the ν(SO) stretching vibrations.

According to the X-ray structure analysis data, the Ni–S and Ni–C bond lengths are 2.1319(5) and 1.885(2) Å, respectively (Fig. 1). These values are shorter than the sums of covalent radii: $r_{Ni} + r_S = 2.29$, $r_{Ni} + r_C = 1.97$ Å [15]. For the thiolate phosphine complexes CpNi($PPh_3$)SPh [16] and CpNi($PPh_3$)S($p$-$C_6H_4$F) [17], the Ni–S bond lengths are 2.191 and 2.199 Å, respectively, whereas this bond length in the carbene complex

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

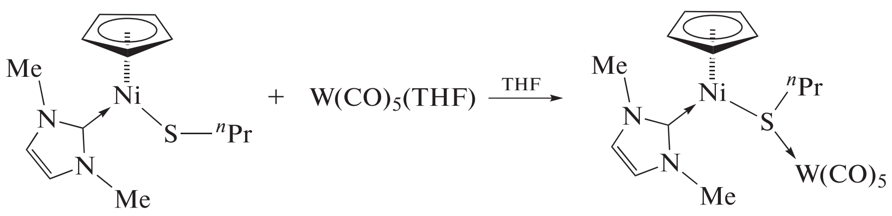
| Parameter | Value | | |
|---|---|---|---|
| | **I** | **II** | **III** |
| *FW* | 327.08 | 618.98 | 786.35 |
| Radiation (λ, Å) | Mo$K_\alpha$ (λ = 0.71073) | | |
| Temperature, K | 100(2) | 100(2) | 150(2) |
| Crystal system | Orthorhombic | Triclinic | Orthorhombic |
| Space group | *Pbca* | $P\bar{1}$ | $P2_12_12_1$ |
| *a*, Å | 8.0066(6) | 10.0044(5) | 8.4555(9) |
| *b*, Å | 12.944(1) | 14.4617(8) | 14.635(2) |
| *c*, Å | 28.077(2) | 16.2778(9) | 18.323(2) |
| α, deg | 90 | 88.8835(8) | 90 |
| β, deg | 90 | 75.9867(7) | 90 |
| γ, deg | 90 | 71.4052(7) | 90 |
| *V*, Å$^3$ | 2909.9(4) | 2161.4(2) | 2267.3(4) |
| *Z* | 8 | 4 | 4 |
| $\rho_{\text{calcd}}$, g/cm$^3$ | 1.493 | 1.902 | 2.304 |
| μ, mm$^{-1}$ | 1.476 | 6.315 | 5.462 |
| *F*(000) | 1376.0 | 1200.0 | 1472.0 |
| Scan range over θ, deg | 5.804–54.936 | 4.064–61.068 | 4.446–59.982 |
| Scan mode | ω | | |
| Independent reflections ($N_1$) | 3339 ($R_{\text{int}}$ = 0.0564) | 13097 ($R_{\text{int}}$ = 0.0299) | 6569 ($R_{\text{int}}$ = 0.0490) |
| Reflections with $I > 2\sigma(I)$ ($N_2$) | 2825 | 10647 | 5900 |
| Number of refined parameters | 175 | 511 | 246 |
| GOOF ($F^2$) | 1.092 | 1.005 | 0.981 |
| $R_1$ for $N_2$ | 0.0394 | 0.0253 | 0.0301 |
| $wR_2$ for $N_1$ | 0.0864 | 0.0545 | 0.0559 |
| $\Delta\rho_{\max}/\Delta\rho_{\min}$, *e* Å$^{-3}$ | 0.39/–0.46 | 1.33/–1.12 | 0.87/–0.58 |

CpNi($Mes_2$Im)[S(*p*-$C_6H_4$OMe)] is 2.192 Å [18]. Thus, the Ni–S bond in complex **I** is shortened over the corresponding values for the thiolate complexes, which can be explained by electron density donating from the metal to the antibonding orbitals of the S–O bond.



**Scheme 2.**

To synthesize heterometallic complex **II** ($\eta^5$-$C_5H_5$)Ni($Me_2$Im)$S^n$Pr, its reaction with the adduct W$(CO)_5$(THF) obtained by the irradiation of tungsten carbonyl in THF was used (Scheme 3).



**Scheme 3.**

The coordination of sulfur by tungsten makes the complex to be unstable in air. The complex was isolated as orange prismatic crystals. The stretching vibration frequencies of the CO groups in the IR spectrum are 2058, 1965, 1895, and 1873 cm$^{-1}$. According to the X-ray structure analysis data (Fig. 2), the Ni–S and W–S bond lengths in complex **II** are 2.1933(7) and 2.5797(7) Å, respectively. The Ni–C bond with the carbene ligand changes insignificantly compared to sulfone complex **I** and is equal to 1.882(3) Å, which indicates an insignificant influence of other substituents on the metal–carbene bond.

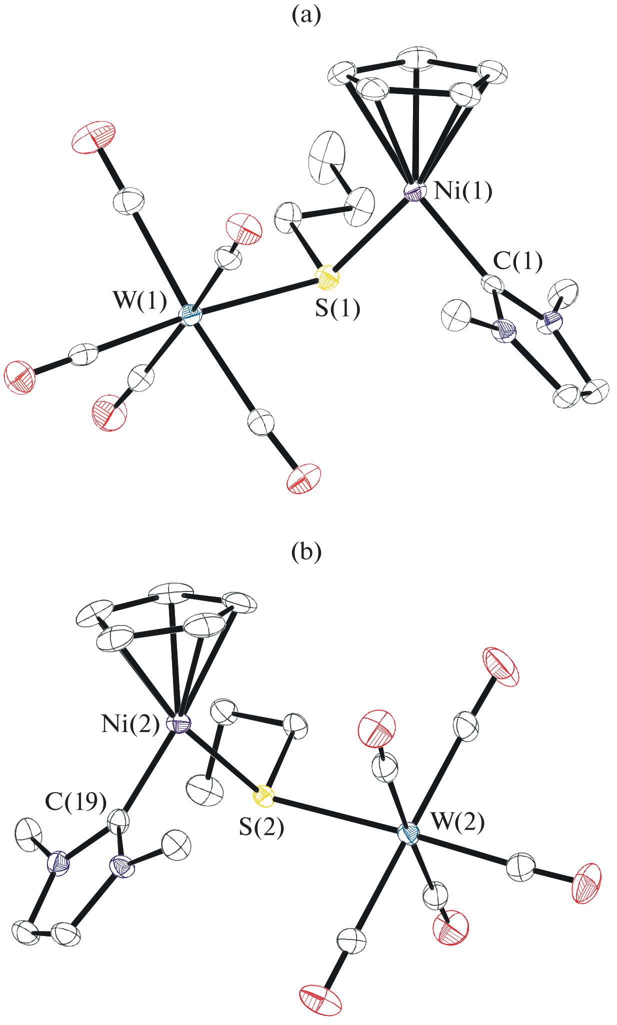
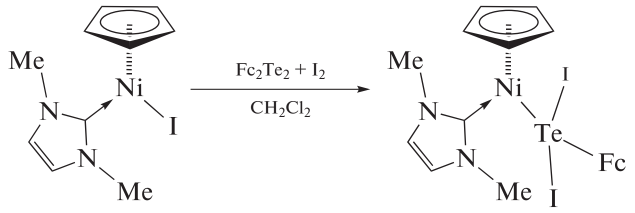


**Fig. 2.** Molecular structure of complex **II**. Selected bond lengths and angles: W(1)–S(1) 2.5797(7), W(2)–S(2) 2.5866(6), Ni(1)–S(1) 2.1933(7), Ni(2)–S(2) 2.1951(7), Ni(1)–C(1) 1.882(3), Ni(2)–C(19) 1.879(3) Å and Ni(1)S(1)W(1) 109.66(3)°, Ni(2)S(2)W(2) 112.69(3)°. Hydrogen atoms are omitted for clarity.

Another method for the preparation of the heterometallic nickel complex is the insertion of ferrocenyltellurium iodide (FcTeI) at the halogen–metal bond, which was earlier observed in the ($\eta^5$-$C_5H_5$)Fe$(CO)_2$I [19] and ($\eta^4$-$C_4Me_4$)Co$(CO)_2$I complexes [20]. For example, new heterometallic complex **III** containing the terminal telluroferrocenyl iodide fragment was obtained by the reaction of the known nickel carbene complex ($\eta^5$-$C_5H_5$)Ni($Me_2$Im)I with FcTeI (Scheme 4).



**Scheme 4.**

In the structure of complex **III** (Fig. 3), the Ni–Te bond (2.4407(8) Å) is strongly shortened compared to the sum of covalent radii ($r_{Ni} + r_{Te} = 2.62$ Å) and two Te–I bonds equal to 2.9686(6) and 3.0015(6) Å, on the contrary, are elongated ($r_{Te} + r_I = 2.77$ Å). Such bond lengths are explained by the backward donation of the lone electron pair of nickel to the tellurium atom and the simultaneous antibonding of the Te–I bonds.

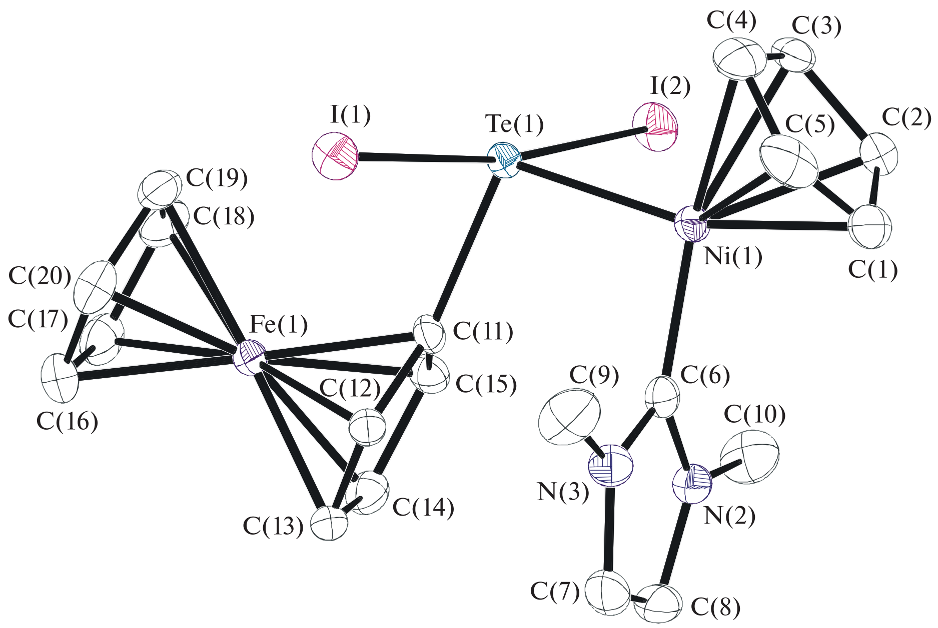


**Fig. 3.** Molecular structure of complex **III**. Selected bond lengths and angles: Ni(1)–C(6) 1.873(6), Ni(1)–Te(1) 2.4407(8), Te(1)–I(1) 2.9686(6), Te(1)–I(2) 3.0015(6), C(6)–N(2) 1.356(8), C(6)–N(3) 1.360(8) Å and Ni(1)Te(1)I(1) 96.08(2)°, Ni(1)Te(1)I(2) 90.55(2)°, I(1)Te(1)I(2) 171.044(18)°. Hydrogen atoms are omitted for clarity.

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