

Distorted Square Planar Ni(II)–Chalcogenolate Carbonyl Complexes [Ni(CO)(SPh)_n(SePh)_{3-n}][−] (n = 0, 1, 2): Relevance to the Nickel Site in CO Dehydrogenases and [NiFeSe] Hydrogenase

Wen-Feng Liaw,^{*,†} Yih-Chern Horng,[†] Der-Shiaw Ou,[†]
Chao-Yi Ching,[†] Gene-Hsiang Lee,[‡] and Shie-Ming Peng[§]

Department of Chemistry, National Changhua
University of Education, Changhua 50058, Taiwan
Instrumentation Center
National Taiwan University, Taipei, Taiwan
Department of Chemistry, National
Taiwan University, Taipei 10764, Taiwan

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The chemistry of transition metal selenolate/thiolate complexes has been actively pursued, motivated primarily by bonding diversity, perspectives of reactivity,¹ and, in particular, the relevance of such complexes (e.g., Fe–thiolate, Ni–thiolate, and Fe–Ni–chalcogenolate complexes) to biomimetic chemistry.² The structure of the [NiFeSe] hydrogenase from *D. baculatus*, determined by XAS studies, revealed that the nickel is ligated to one Se atom at 2.44 Å, one to two S/Cl atoms at 2.17 Å, and three to four N/O atoms at 2.06 Å.³ A more sulfur-rich environment is found for nickel in the recently reported X-ray crystal structure of [NiFe] hydrogenase isolated from *D. gigas*, which indicated as well that the Ni ion in the hydrogenase is in a binuclear metal site bridged by thiocysteines.⁴ In CODH, the oxidation of CO to CO₂ and acetyl-CoA synthesis from CO, CH₃ group, and CoA occur at coupled [Ni–X–Fe] centers,⁵ and both nickel and iron have been proposed as binding sites of CO.^{6,7} Additionally, excess CO is known to inhibit activity in both CODH and in [NiFe] hydrogenase, hence precedents for Ni–CO binding and their spectral characteristics are desirable.^{2,5} Recently, the five-coordinate Ni(I)–chalcogenolate carbonyl complex [Ni(DAPA)(EPh)₂(CO)][−] (E = S, Se)⁸ and the first five-coordinate Ni(II) thiolate carbonyl complex [Ni(PS3*)(CO)][−] (PS3* = tris(3-phenyl-2-thiophenyl)phosphine) were reported.⁹ In spite of the large number of Ni(0) carbonyl complexes known and one series of square planar Ni(II) carbonyls suggested,¹⁰ no example of CO bonded to Ni(II) in a square planar geometry has been structurally characterized.¹¹

Recent work in this laboratory has shown that *cis*-[Mn(CO)₄(ER)₂][−] (E = Se, Te; R = phenyl, alkyl) serve as chelating ligands and selenolate ligand-transfer reagents in the syntheses

of heterometallic chalcogenolate species^{12a,b} and that *fac*-[Fe(CO)₃(SePh)₃][−] exhibits a unique coordination behavior toward divalent nickel ion.^{12 c–e} Our efforts toward the preparations of Ni(II)–selenolate and Ni(II)–mixed–chalcogenolate carbonyl complexes providing the first example of binding of CO at a square planar Ni(II) center surrounded by biological selenolate/thiolate ligands exploits use of *fac*-[Fe(CO)₃(SePh)₃][−] as a selenolate ligand-transfer reagent.

A mixture of [CpNi(CO)]₂ (0.0608 g, 0.2 mmol) and (PhSe)₂ (0.062 g, 0.2 mmol) was added to *fac*-[PPN][Fe(CO)₃(SePh)₃] (0.458 g, 0.4 mmol) in acetonitrile (or THF) solution, and the reaction mixture was stirred under N₂ at 30 °C. The reaction mixture finally led to the isolation of dark green [PPN][Ni(CO)(SePh)₃] precipitate (0.341 g, 83%)¹³ on addition of diethyl ether and the diethyl ether-soluble green CpFe(CO)₂(SePh) (0.107 g, 80%).¹⁴ The complex [PPN][Ni(CO)(SePh)₃] is insoluble in hexane and ethyl ether and forms slightly air-sensitive solutions in THF and CH₃CN. Crystals suitable for X-ray analysis were obtained by tetrahydrofuran/hexane diffusion. The sequences of reaction given in Scheme 1 reasonably accounts for the observation. The oxidative addition of diphenyl diselenide across the Ni–Ni bond,¹⁵ bridge-breaking, and displacement of a coordinated C₅H₅[−] ligand by an incoming tridentate metallo ligand *fac*-[Fe(CO)₃(SePh)₃][−] must be accompanied by cyclopentadienyl ligand-transfer from Ni(II) to Fe(II),¹⁶ concomitant Fe(II)–SePh bond cleavage, and a labile carbonyl ligand shifting from Fe(II) to Ni(II) (CpNi(CO)(SePh), thermally unstable, converted into [CpNi(μ-SePh)]₂ at room temperature, and the addition of *fac*-[Fe(CO)₃(SePh)₃][−] to [CpNi(μ-SePh)]₂ in THF led to formation of [Ni(CO)(SePh)₃][−] and CpFe(CO)₂(SePh).^{12a} These results establish that the same stoichiometric quantities of CpFe(CO)₂(SePh) are formed concurrently with [PPN][Ni(CO)(SePh)₃].

Complex [Ni^{II}(CO)(SePh)₃][−] exhibits a ν_{CO} IR band at 2023 cm^{−1} which compares well to the ν_{CO} bands of pentacoordinate Ni(I)/Ni(II) carbonyl complexes such as [Ni(NS₃^{tBu})(CO)][−][BPh₄][−] (2026 cm^{−1}),¹⁷ [Ni(DAPA)(SePh)₂(CO)][−] (2024 cm^{−1}),⁸ and

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(13) [PPN][Ni(CO)(SePh)₃]: IR (ν_{CO}) (THF): 2023 s cm^{−1}. ¹H NMR (CD₃CN): δ 7.04–7.61 (m) (Ph) ppm. ¹³C NMR (CD₃CN): δ 134.5, 133.3, 133.2, 133.0, 130.4, 130.3, 130.2, 130.1, 129.2, 129.0, 125.7 (Ph) ppm. Absorption spectrum (THF) [λ_{max}, nm (ε, M^{−1} cm^{−1}): 337(16 710), 419(1979) (sh), 569(952). Anal. Calcd for C₅₅H₄₅ONP₂Se₃Ni: N, 1.28; C, 60.41; H, 4.15. Found: N, 1.34; C, 60.20; H, 4.13. The complex [PPN][Ni(CO)(SePh)₃] crystallized in triclinic space group P1 with a = 10.117(4) Å, b = 15.780(4) Å, c = 16.425(5) Å, α = 72.50(3)°, β = 86.78(3)°, γ = 87.26(3)°, chemical formula = C₅₅H₄₅ONP₂NiSe₃, fw = 1093.49, V = 2495.5(14) Å³, Z = 2, d_{calc} = 1.455 g cm^{−3}, λ = 0.7107, F(000) = 1101, and T = 298 K; final R = 0.044 and R_w = 0.040.

(14) (a) CpFe(CO)₂(SePh): IR (ν_{CO}) (THF): 2022 s, 1974 s cm^{−1}. ¹H NMR (CD₃CN): δ 5.03 (s) (Cp), 7.06–7.59 (m) (Ph) ppm. ¹³C NMR (CD₃CN): δ 86.71 (Cp), 137.0, 129.1, 126.4 (Ph), 215.8 (CO) ppm. The complex CpFe(CO)₂(SePh) crystallized in monoclinic space group P2₁/c with a = 9.554(3) Å, b = 11.479(3) Å, c = 11.775(6) Å, β = 104.58(3)°, V = 1249.8(8) Å³, Z = 4, d_{calc} = 1.770 g cm^{−3}, λ = 0.7107, F(000) = 657, and T = 298 K; final R = 0.063 and R_w = 0.062. (b) Schermer, E. D.; Baddley, W. H. *J. Organometal. Chem.* **1971**, *27*, 83.

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[§] Department of Chemistry, National Taiwan University.

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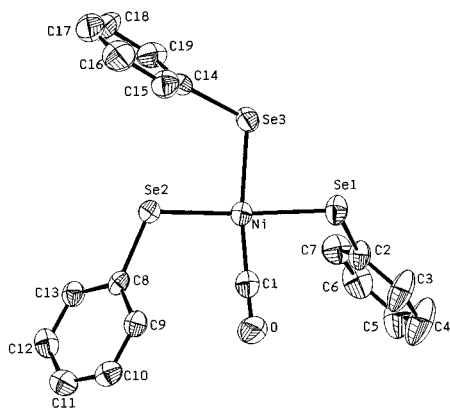
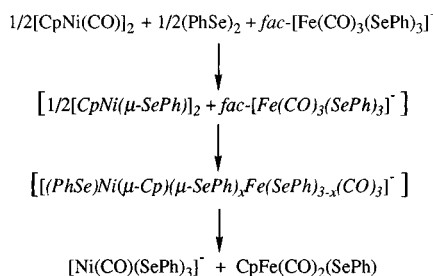


Figure 1. ORTEP drawing and labeling scheme of the $[\text{Ni}(\text{CO})(\text{SePh})_3]^-$ anion. Selected bond distances (Å) and angles (deg): Ni–Se(1), 2.349(1); Ni–Se(2), 2.293(1); Ni–Se(3), 2.309(2); Ni–C(1), 1.729(8); C(1)–O, 1.128(9); Se(1)–C(2), 1.928(7); Se(2)–C(8), 1.902(7); Se(3)–C(14), 1.928(6); Se(1)–Ni–Se(2), 173.84(5); Se(1)–Ni–Se(3), 83.99(5); Se(1)–Ni–C(1), 87.17(23); Se(2)–Ni–Se(3), 92.79(5); Se(2)–Ni–C(1), 96.35(23); Se(3)–Ni–C(1), 170.44(24); Ni–C(1)–O, 177.1(7); Ni–Se(1)–C(2), 107.95(20); Ni–Se(2)–C(8), 112.30(17); Ni–Se(3)–C(14), 112.29(20).

Scheme 1



$[\text{Ni}(\text{PS}^3)(\text{CO})]^-$ (2029 cm^{-1}).⁹ When a THF solution of $[\text{Ni}^{\text{II}}(\text{CO})(\text{SePh})_3]^-$ is purged with ^{13}CO , the IR ν_{CO} peak at 2023 cm^{-1} immediately shifts to a single absorbance at 1976 cm^{-1} . The magnitude 47 cm^{-1} of the isotopic shift is consistent with the calculated position, based only on the difference in masses between ^{12}CO and ^{13}CO .

The molecular structure of $[\text{Ni}(\text{CO})(\text{SePh})_3]^-$ is depicted in Figure 1. Nickel is best described as existing in a distorted square planar coordination environment surrounded by one carbonyl and three terminal phenylselenolates in $[\text{Ni}(\text{CO})(\text{SePh})_3]^-$ with Se(3)–Ni–C(1) = 170.44(24)°, Se(1)–Ni–Se(2) = 173.84(5)°, Se(1)–Ni–Se(3) 83.99(5)°, and Se(2)–Ni–Se(3) = 92.79(5)°. The Ni(II)–Se bond lengths range from 2.293(1) to 2.349(1) Å (average = 2.317(2) Å). These are shorter than the Ni(II)–Se distances reported in tetrahedral $[\text{Ni}(\text{SePh})_4]^{2-}$ (Ni–Se_{av} = 2.401(3) Å),¹⁸ five-coordinate $[\text{Ni}(\text{DAPA})(\text{SePh})_2]$ (Ni–Se_{av} = 2.420(1) Å),⁸ and $[\text{Ni}(\text{dmp})(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{Se})_2]$ (Ni–Se_{av} = 2.362(3) Å),¹⁹ but longer than that observed for planar $[\text{Ni}(\text{Se}(\text{CH}_2)_2\text{N}(\text{Me})(\text{CH}_2)_2\text{Se})_2]$, average Ni(II)–Se = 2.295(6) Å.²⁰ The $[\text{Ni}^{\text{II}}(\text{CO})(\text{SePh})_3]^-$ exhibits a shorter Ni–CO distance (1.729(8) Å) than $[\text{Ni}(\text{NS}_3^{\text{tBu}})(\text{CO})]^+$ (1.85(1) Å)¹⁷ and $[\text{Ni}(\text{PS}^3)(\text{CO})]^-$ (1.75(3) Å (PS³ = tris(3-phenyl-2-thiophenyl)phosphine)).⁹ The terminal Fe(II)–SePh bond length of 2.413(3) Å in $\text{CpFe}(\text{CO})_2(\text{SePh})$ is shorter than

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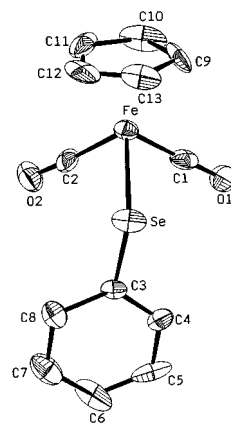


Figure 2. ORTEP drawing and labeling scheme of the $\text{CpFe}(\text{CO})_2(\text{SePh})$. Selected bond distances (Å) and angles (deg): Fe–Se, 2.413(3); Fe–C(1), 1.731(15); Fe–C(2), 1.758(14); Fe–C(9), 2.090(14); Fe–C(10), 2.043(16); Fe–C(11), 2.073(16); Fe–C(12), 2.036(16); Fe–C(13), 2.072(14); Se–Fe–C(1), 90.3(5); Se–Fe–C(2), 91.8(5); C(1)–Fe–C(2), 94.6(6); Fe–Se–C(3), 105.8(3).

the average Fe(II)–SePh bond length of 2.459(2) Å in *fac*- $[\text{Fe}(\text{CO})_3(\text{SePh})_3]^-$ (Figure 2).^{12c}

The reaction of $[\text{Ni}(\text{CO})(\text{SePh})_3]^-$ with 1 equiv of $(\text{PhS})_2$ in THF results in immediate formation of the extremely air-sensitive dark green $[\text{Ni}(\text{CO})(\text{SPh})(\text{SePh})_2]^-$ (compared to $[\text{Ni}(\text{CO})(\text{SePh})_3]^-$) in 87% yield under N_2 at 25 °C.²¹ When the air-sensitive $[\text{Ni}(\text{CO})(\text{SPh})(\text{SePh})_2]^-$ solution was exposed to ^{13}CO , an absorbance at 1982 cm^{-1} appeared within 10 min. Reappearance of the 2028 cm^{-1} band on removal of the ^{13}CO and replacement with ^{12}CO atmosphere demonstrated reversibility of CO ligand lability of $[\text{Ni}(\text{CO})(\text{SPh})_n(\text{SePh})_{3-n}]^-$ ($n = 0, 1$) complexes.²² In a similar fashion, $[\text{Ni}(\text{CO})(\text{SePh})_3]^-$ was reacted with $(\text{PhS})_2$ (1:2 molar ratio) in THF under a nitrogen atmosphere, and the reaction mixture finally led to the isolation of dark green $[\text{Ni}(\text{CO})(\text{SPh})_2(\text{SePh})]^-$.^{23,24}

Such structural models as $[\text{Ni}(\text{CO})(\text{SPh})_n(\text{SePh})_{3-n}]^-$ ($n = 0, 1, 2$) may be appreciated as possibilities for intermediates in biological reaction pathways or as structures important to CO-inhibitory processes in Ni-containing enzymes.²⁵ In our hands they serve as precursors for synthetic goals of preparing Ni–Fe heterometallics in biological-type ligation settings, and reactivity studies of these Ni(II)–chalcogenolate carbonyl complexes are underway.

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Supporting Information Available: Tables of crystal data and experimental conditions for the X-ray studies, atomic coordinates and B_{eq} values, complete listings of bond lengths and bond angles, and anisotropic temperature factors for $[\text{PPN}][\text{Ni}(\text{CO})(\text{SePh})_3]$ and $\text{CpFe}(\text{CO})_2(\text{SePh})$ (7 pages). See any current masthead page.

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