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Cyclopentadienylnickel(II) Thiolato and Selenolato Complexes. Synthesis, Characterization, and X-ray Structure of (η^5-C_5H_5)Ni(SePh)(PPh_3)

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Summary: The treatment of Cp$^\#$NiX(PPh$_3$) (Cp$^\#$ = C$_5$H$_5$ (Cp), C$_5$H$_4$Me, (Cp′); X = Cl, Br, I) with benzenethiol or benzeneselenol, in the presence of Et$_3$N, gave Cp$^\#$Ni(EPh)(PPh$_3$) (E = S, Se). The complex CpNi(SePh)(PPh$_3$) can also be prepared from in situ generated [CpNi(μ-SePh)]$_2$ and PPh$_3$. The compound crystallizes in the triclinic space group P$\bar{1}$ with the following cell parameters: a = 9.610(1) Å, b = 11.480(2) Å, c = 11.536(2) Å, α = 79.74(2)°, β = 73.98(1)°, γ = 83.45(1)°, V = 1201 Å^3, and Z = 2. The final least-squares refinement gave R = 0.0339 and R_w = 0.0356 for 4497 reflections.

Introduction

Access to cyclopentadienylruthenium chemistry has been greatly aided by the use of CpRuCl(PPh$_3$)$_2$ as a starting material.[1] Rauchfuss[2] and Shaver[3] have independently utilized this ruthenium starting material as an entry into cyclopentadienylruthenium chalcogenide and organochalcogenate chemistry. In comparison, however, the isoelectronic CpNiX(PPh$_3$) has not been extensively investigated. The use of CpNiX(PPh$_3$) to synthesize cyclopentadienylnickel chalcogenide and organochalcogenate complexes is even more limited.[4–6]

For nickel two main reaction types have allowed cyclopentadienylnickel compounds to be prepared from CpNiX(PPh$_3$). Insertion of GeCl$_2$ into the Ni–halide bond produces CpNi(PPh$_3$)(GeCl$_3$).[7] The second reaction type, anion exchange, is the replacement of the halide atom by the desired ligand when it reacts in its salt form with CpNiCl(PPh$_3$). For this type, in situ generated [Et$_3$NH][SR] (R = C$_6$H$_5$, C$_6$H$_4$Me-4) and LiP(SiMe$_3$)$_2$ react to give CpNi(SR)(PPh$_3$)[6] and CpNi{P(SiMe$_3$)$_2$}(PPh$_3$),[8] respectively.

As part of our continuing investigation of the chemistry of CpNiX(PPh$_3$), we report the syntheses of Cp$^\#$Ni(EPh)(PPh$_3$) using the anion exchange route. In addition, we have synthesized CpNi(SePh)(PPh$_3$) by the method of Taube et al.,[5] which involves the reaction of in situ generated [CpNi(μ-SePh)]$_2$ with PPh$_3$.

Results and Discussion

Synthesis of CpNi(SePh)(PPh$_3$) has been performed by two methods. First, base-promoted deprotonation of benzeneselenol gave the product in moderate yield (eq 1). This is similar to our method for the synthesis of CpNi(SPh)(PPh$_3$)[6].

$$\mathrm{CpNiBr(PPh_3) + HSePh + Et_3N \rightarrow CpNi(SePh)(PPh_3) + Et_3NHBr} \quad (1)$$

The second method involves the reaction of [CpNi(μ-SePh)]$_2$ with PPh$_3$. This route is analogous to that of Taube and co-workers for the preparation of CpNi(SPh)(PPh$_3$).[5] Our efforts to isolate [CpNi(μ-SePh)]$_2$, using the procedure described in the literature for [CpNi(μ-SPh)]$_2$,[9] were unsuccessful. When a toluene solution of Cp$_2$Ni was reacted with HSePh at room temperature, the expected product, [CpNi(μ-SePh)]$_2$, decomposed on exposure to air. This behavior is in contrast to that of the air-stable [CpNi(μ-SPh)]$_2$. When a toluene solution of [CpNi(μ-SePh)]$_2$ was refluxed under nitrogen, a black insoluble solid was isolated, indicating that [CpNi(μ-SePh)]$_2$ is unstable to heat. However, when this dimer was generated in solution from the reaction of Cp$_2$Ni and HSePh, addition of PPh$_3$ gave the air-stable CpNi(SePh)(PPh$_3$) in moderate yield (eq 2).

$$\mathrm{Cp_2Ni + HSePh} \xrightarrow[-\mathrm{CpH}]{} {}^{1}/_{2}\ \text{“[CpNi(}\mu\text{-SePh)]}_2\text{”} \xrightarrow{\mathrm{PPh_3}} \mathrm{CpNi(SePh)(PPh_3)} \quad (2)$$

Addition of either HSPh or HSePh to in situ generated Cp′NiBr(PPh$_3$), as in eq 1, gave Cp′Ni(SPh)(PPh$_3$) and Cp′Ni(SePh)(PPh$_3$), respectively. All the organochalcogenide products were dark green in the solid state but were dark brown in solution. The color of the solutions was the same in polar as well as in nonpolar solvents such as toluene, THF, and CH$_2$Cl$_2$. The NMR spectra of the complexes clearly established the presence of the cyclopentadienyl ring, PPh$_3$, and EPh ligands, and the complexes appear to have the same structure in solution as in the solid state. On the basis of above, it is unlikely that the different colors observed in solution and in the solid state are solvent-related. We, however, have been unable to establish the source of these color differences. One interesting aspect of the ^{1}H NMR spectra of the

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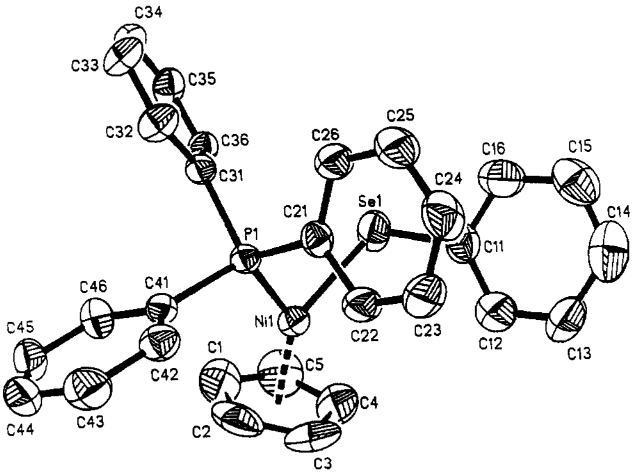

Figure 1. Structure of (η^5-C_5H_5)Ni(SePh)(PPh_3).

methylcyclopentadienyl complexes is the observation of through-space coupling between the methyl group of the cyclopentadienyl ligand and the phosphorus of the PPh_3 group. The coupling constants are 2.74 Hz for Cp′Ni(SPh)(PPh_3) and 2.01 Hz for Cp′Ni(SePh)(PPh_3). The ^{13}C NMR spectra showed all cyclopentadienyl and methyl carbons as singlets, with no observable coupling to the PPh_3. Larger coupling constants of 4.0–4.5 Hz have been observed by Ballester et al.[10] for Cp′NiX(PPh_3) (X = Cl, Br, SCN). The analogous iodo complex Cp′NiI(PPh_3) showed no coupling between the methyl protons and the phosphine, and its solid-state structure has the methyl of the Cp′ directed away from the phosphine. It is therefore conceivable that, at least in solution, the structures of Cp′Ni(SPh)(PPh_3) and Cp′Ni(SePh)(PPh_3) would have the methyl groups on the same side as the phosphine, though this would be a less favorable structure in the solid state for steric reasons. We have not been able to obtain X-ray-quality crystals to establish the solid-state structure unequivocally.

The molecular structure of CpNi(SePh)(PPh_3) was determined by X-ray crystallography and is shown in Figure 1 and Table 2, which gives selected bond distances and angles. The overall geometry around the nickel is similar to that previously found for CpNi(SPh)(PPh_3).[6] The distance from the centroid of the cyclopentadienyl rings to the nickel in both molecules is 1.748 Å; however, the Ni–P distances vary slightly. The Ni–Se bond distance of 2.303(1) Å is comparable to that found in [Ni(μ-SePh)(SePh)(Me_2Phen)]$_2$ and other related species,[11] which have Ni–Se bond lengths ranging from 2.340(2) to 2.605(1) Å. It is also comparable to the bond length of 2.301(1) Å found in [Cp*Ni(μ-SePh)]$_2$.[12] The bond angles around the nickel atom are essentially the same for CpNi(SePh)(PPh_3) and CpNi(SPh)(PPh_3).

Thermogravimetric analysis of CpNi(SePh)(PPh_3), Cp′Ni(SePh)(PPh_3), and Cp′Ni(SPh)(PPh_3) showed abrupt weight loss in the thermograms at 180–250 °C. This corresponds to a combined weight loss of EPh and PPh_3 for each compound. However, the first-derivative plots of the thermograms are indicative of the loss of two different species, one below 200 °C and the other above 200 °C. Our inability to observe two distinct weight losses may be due to the heating rate used. Nevertheless, it is clear from the thermogravimetric experiments that the decomposition of the complexes Cp$^{\#}$Ni(EPh)(PPh_3) leads to loss of EPh and PPh_3.

Table 1. Crystallographic Data for CpNi(SePh)(PPh_3)

formula	$C_{29}H_{25}NiPSe$
space group	$P\bar{1}$
a, Å	9.610(1)
b, Å	11.480(2)
c, Å	11.536(2)
α, deg	79.74(2)
β, deg	73.98(1)
γ, deg	83.45(1)
V, Å^3	1201
Z	2
F(000)	552
d_{calc}, g/cm^3	1.50
cryst size, mm	0.40 × 0.35 × 0.30
μ(Mo K_α), cm^{-1}	23.9
data collecn instrument	Nicolet R3mV
radiation	Mo K_α (λ = 0.710 73 Å)
orientation rflns: no.; range (2θ), deg	30; $17 \le 2\theta \le 29$
temp, K	293
no. of data meas	4497
no. of unique data	4224
no. of unique with $I \ge 3.0\sigma(I)$	3228
no. of params	289
R^a	0.0339
$R_w{}^b$	0.0356
weighting scheme	$w^{-1} = \sigma^2(F) + 0.00018F^2$
largest shift/esd, final cycle	0.001
largest peak, e/Å^3	0.31

[a] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $R_w = \sum w^{1/2}[|F_o| - |F_c|]/\sum_w{}^{1/2}|F_o|$.

Table 2. Selected Bond Distances and Bond Angles for CpNi(SePh)(PPh_3)

Bond Distances (Å)			
Ni–P	2.136(1)	Ni–Se	2.303(1)
Ni–Cp^a	1.748	P–C(21)	1.820(4)
P–C(31)	1.817(3)	P–C(41)	1.833(3)
Se–C(11)	1.918(5)		
Bond Angles (deg)			
Cp–Ni–P	136.4	Cp–Ni–Se	132.3
Se–Ni–P	91.4(1)	Ni–Se–C(11)	107.9(1)
Ni–P–C(21)	111.8(1)	Ni–P–C(31)	117.9(1)
Ni–P–C(41)	113.3(1)	C(21)–P–C(31)	107.6(2)
C(21)–P–C(41)	104.9(1)	C(31)–P–C(41)	100.1(2)

[a] The distance from the centroid of the ring to the nickel atom.

Experimental Section

Materials and Instrumentation. All compounds described in this report are air stable, but reactions were performed under a nitrogen atmosphere to avoid air-sensitive intermediates reacting with oxygen. All workup procedures were, however, performed in air. Solvents were of analytical grade and were used without further purification. Benzeneselenol and benzenethiol (Fluka) were used as received. Triethylamine was distilled from, and stored over, NaOH. CpNiBr(PPh_3) and Cp_2Ni were prepared by the literature methods.[13] Infrared spectra were recorded on a Pye Unicam SP3-300S as Nujol mulls between KBr plates. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 300 and referenced to residual $CHCl_3$ for ^1H (δ 7.26) and ^{13}C (δ 77.0) and to 85% H_3PO_4 for ^{31}P. Thermal analyses were performed on a Perkin-Elmer 7 Series/Unix TGA7 system. Elemental analyses were performed by CHN Analysis Limited, Leicester, England.

Synthesis of CpNi(SePh)(PPh_3). Method A. To a solution of CpNiBr(PPh_3) (1.00 g, 2.15 mmol) in toluene (100

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mL) was added HSePh (0.23 mL, 2.15 mmol), followed by $\mathrm{Et_3N}$ (1 mL). The purple solution turned brown, and the mixture was stirred for 2 h. The mixture was filtered and the solvent removed from the filtrate in vacuo to give a green residue. Recrystallization from a $\mathrm{CH_2Cl_2}$–hexane mixture gave 0.82 g (70%) of dark green crystalline CpNi(SePh)($\mathrm{PPh_3}$). Anal. Calcd for $\mathrm{C_{29}H_{25}PSeNi}$: C, 64.25; H, 4.65. Found: C, 63.95; H, 4.67. ^{1}H NMR (δ): 7.71–7.64 (m, 6H, $\mathrm{PPh_3}$); 7.49–7.32 (m, 9H, $\mathrm{PPh_3}$); 7.51 (d, J_{HH} = 6.99 Hz, 2H, SePh); 6.99–6.89 (m, 3H, SePh); 5.05 (s, 5H, Cp). ^{13}C{^{1}H} NMR (δ): 144.3 (s), 135.6 (s), 133.8 (d, J_{CP} = 10.79 Hz), 128.2 (d, J_{CP} = 10.48 Hz) ($\mathrm{PPh_3}$); 133.2 (s), 130.1 (s), 127.5 (s), 123.9 (s) (SePh); 93.7 (s, Cp). ^{31}P{^{1}H} NMR (δ): 39.24 ($\mathrm{PPh_3}$). IR (Nujol mull, cm^{-1}): 1575 (w), 1440 (sh), 1350 (w), 1160 (w), 1105 (w), 1030 (w), 1010 (w), 845 (m), 800 (s), 765 (m), 745 (s), 710 (s), 700 (s), 540 (s), 515 (m), 495 (m), 460 (w).

Method B. Neat HSePh (0.25 mL, 2.34 mmol) was added to a solution of $\mathrm{Cp_2Ni}$ (0.50 g, 2.65 mmol) in toluene (100 mL). The green solution turned brown and was stirred at room temperature for 1 h. Adding $\mathrm{PPh_3}$ (0.70 g, 2.65 mmol) to the mixture and stirring for 20 h gave a dark brown solution. A small amount of a brown insoluble solid was removed by filtration and the filtrate evaporated to a green residue. Recrystallization from $\mathrm{CH_2Cl_2}$–hexane produced dark green crystalline CpNi(SePh)($\mathrm{PPh_3}$). Yield: 0.80 g, 63% based on HSePh.

Synthesis of Cp′Ni(SPh)(PPh$_3$). To a solution of Cp′NiBr($\mathrm{PPh_3}$), generated from $\mathrm{NiBr_2(PPh_3)_2}$ (2.00 g, 2.69 mmol) and KCp′ (2.69 mmol), were added HSPh (0.26 mL, 2.54 mmol) and $\mathrm{Et_3N}$ (2 mL). The purple solution turned dark brown immediately and was stirred for 1 h. The resultant mixture was evaporated and the residue extracted with toluene (75 mL). After the toluene extract was concentrated to a green oil, the residue was crystallized from $\mathrm{CH_2Cl_2}$–hexane to give analytically pure Cp′Ni(SPh)($\mathrm{PPh_3}$). Yield: 0.60 g, 50% based on HSPh. Anal. Calcd for $\mathrm{C_{30}H_{27}PSNi}$: C, 70.75; H, 5.34. Found: C, 70.79; H, 5.48. ^{1}H NMR (δ): 7.68–7.61 (m, 6H, $\mathrm{PPh_3}$); 7.33–7.30 (m, 9H, $\mathrm{PPh_3}$); 7.32 (d, J_{HH} = 6.09 Hz, 2H, SPh); 6.88–6.80 (m, 3H, SPh); 5.30 (s, 2H, Cp′); 4.58 (s, 2H, Cp′); 1.49 (d, J_{HP} = 2.74 Hz, 3H, Cp′). ^{13}C{^{1}H} NMR (δ): 145.0 (s), 133.7 (d, J_{CP} = 11.00 Hz), 133.0 (s), 128.2 (d, J_{CP} = 10.01 Hz) ($\mathrm{PPh_3}$); 132.1 (s), 129.9 (s), 126.9 (s), 121.5 (s) (SPh); 111.7 (s), 96.9 (s), 89.1 (s), 13.1 (s) (Cp′). ^{31}P{^{1}H} NMR (δ): 34.7 ($\mathrm{PPh_3}$). IR (Nujol mull, cm^{-1}): 1556 (w), 1430 (s), 1345 (w), 1095 (m), 1020 (w), 1000 (w), 820 (w), 795 (m), 785 (m), 750 (s), 735 (s), 700 (vs), 680 (s), 535 (s), 510 (m), 495 (m), 460 (w), 420 (w).

Synthesis of Cp′Ni(SePh)(PPh$_3$). The procedure and workup were similar to that of Cp′Ni(SPh)($\mathrm{PPh_3}$) with the starting material, Cp′NiBr($\mathrm{PPh_3}$), generated on the same scale using HSePh (0.30 mL, 2.83 mmol) and $\mathrm{Et_3N}$ (2 mL). Yield: 0.64 g, 40%, based on HSePh. Anal. Calcd for $\mathrm{C_{30}H_{27}PSeNi}$: C, 64.79; H, 4.89. Found: C, 64.22; H, 4.87. ^{1}H NMR (δ): 7.70–7.64 (m, 6H, $\mathrm{PPh_3}$); 7.38–7.34 (m, 9H, $\mathrm{PPh_3}$); 7.53 (d, J_{HH} = 7.14 Hz, 2H, SePh); 6.95–6.88 (m, 3H, SePh); 5.11 (s, 2H, Cp′); 4.71 (s, 2H, Cp′); 1.66 (d, J_{HP} = 2.01 Hz, 3H, Cp′). ^{13}C{^{1}H} NMR (δ): 147.0 (s), 133.7 (d, J_{CP} = 10.94 Hz), 128.2 (d, J_{CP} = 10.11 Hz) ($\mathrm{PPh_3}$); 135.0 (s), 130.0 (s), 127.3 (s), 123.3 (s) (SePh); 109.9 (s), 95.8 (s), 90.0 (s), 13.4 (s) (Cp′). IR (Nujol mull, cm^{-1}): 3040 (w), 1565 (w), 1470 (sh), 1430 (s), 1340 (w), 1305 (w), 1185 (m), 1156 (w), 1120 (w), 1090 (s), 1065 (w), 1030 (w), 1015 (w), 995 (w), 830 (w), 795 (m), 780 (m), 750 (s), 730 (s), 720 (m), 700 (vs), 685 (s), 660 (w), 545 (vs), 520 (m), 500 (m), 470 (w), 430 (w).

Crystal Structure Determination of CpNi(SePh)(PPh$_3$). Single crystals of the title compound were obtained by layering a $\mathrm{CH_2Cl_2}$ solution with hexane and keeping the solution at −15 °C. A dark green crystal (0.40 mm × 0.35 mm × 0.30 mm) was mounted on a glass fiber for data collection. Crystallographic data are summarized in Table 1. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 30 reflections taken from a rotation photograph and centered by the diffractometer. The data were corrected for Lorentz and polarization effects and, empirically, for absorption. The structure was solved by direct methods and developed by using alternating cycles of least-squares refinement and difference-Fourier synthesis. The non-hydrogen atoms were refined anisotropically, while hydrogens were placed in idealized positions (C–H = 0.96 Å) and assigned a common isotropic thermal parameter (U = 0.08 Å^2). The final cycle of least-squares refinement included 289 parameters for 3228 variables and did not shift any parameters by more than 0.001 times its standard deviation. The final difference-Fourier map was featureless, with no peaks greater than 0.31 e Å^{-3}. Crystallographic calculations were performed on a MicroVax II computer using the SHELTX PLUS program package.[14]

Thermal Analysis. Thermogravimetric analyses of all complexes were performed on powdered samples (2.34–2.99 mg) under a constantly flowing stream of nitrogen at a flow rate of 20 cm^{-3}/min and a heating rate of 20 °C/min.

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Supplementary Material Available: Figures giving an additional view of the structure of CpNi(SePh(($\mathrm{PPh_3}$) and unit cell packing diagrams of this compound, as well as tables of its positional parameters, all bond lengths and angles, and thermal parameters, and figures detailing the thermogravimetric analyses of CpNi(SePh)($\mathrm{PPh_3}$), Cp′Ni(SePh)($\mathrm{PPh_3}$), and Cp′Ni(SPh)($\mathrm{PPh_3}$) (14 pages). Ordering information is given on any current masthead page.

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