Articles

Bis(cyclopentadienyl)yttrium Complexes of the Ligand $[N(QPPh_2)_2]^-$ (Q = S, Se): Synthesis, Structure, and NMR Properties of $Cp_2Y[\eta^3\text{-}N(QPPh_2)_2]$

Christopher G. Pernin and James A. Ibers*

Department of Chemistry, Northwestern University, Illinois 60208-3113

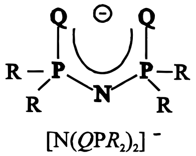
Received May 25, 1999

The compounds $Cp_2Y[\eta^3\text{-}N(QPPh_2)_2]$ (Q = S (**1**), Se (**2**)) have been synthesized in good yield from the protonolysis reaction between Cp_3Y and $HN(QPPh_2)_2$ in tetrahydrofuran. In both compounds, the $[N(QPPh_2)_2]^-$ ligand is bound η^3 to the Y center which, in **1**, represents the first example of that mode of binding for the sulfur-containing ligand. The Y atom is also coordinated to two $(C_5H_5)^-$ ligands and so is formally 9-coordinate. Both **1** and **2** are stable in inert environments for prolonged periods of time. Each is soluble in THF and CH_2Cl_2. ^1H, ^{31}P, ^{77}Se, and ^{89}Y NMR data were collected to lend insight into the solution properties of these molecules. Crystallographic data for **1** (−120 °C): $C_{34}H_{30}NP_2S_2Y$, triclinic, $P\bar{1}$, $a = 9.685(5)$ Å, $b = 12.176(6)$ Å, $c = 13.978(7)$ Å, $\alpha = 87.382(9)°$, $\beta = 87.358(9)°$, $\gamma = 68.689(9)°$, $V = 1533(1)$ Å^3, $Z = 2$, and $R_1(F) = 0.047$ for the 4023 reflections with $I > 2\sigma(I)$. Crystallographic data for **2** (−120 °C): $C_{34}H_{30}NP_2Se_2Y$, triclinic, $P\bar{1}$, $a = 9.745(5)$ Å, $b = 12.222(6)$ Å, $c = 13.930(7)$ Å, $\alpha = 88.024(9)°$, $\beta = 87.380(9)°$, $\gamma = 69.137(9)°$, $V = 1548(1)$ Å^3, $Z = 2$, and $R_1(F) = 0.056$ for the 4324 reflections with $I > 2\sigma(I)$.

Introduction

The inorganic ligands imidodiphosphinochalcogenido, $[N(QPR_2)_2]^-$ (Q = S, Se; R = Me, Ph, Et for example), have recently been the focus of many studies[1−18] (Scheme 1) owing to the structural diversity in the metal complexes they form and their relationship to the organic ligand acetylacetonato (acac). In 1995, Bhattacharyya and co-workers[9−12,17] reported a convenient preparation of these ligands that facilitated these studies. These ligands are known to exhibit a range of binding geometries that depend on the choice of Q, R, and chelated metal.[9,15,17] For example, $[N(SePPh_2)_2]^-$ forms neutral square-planar complexes with Pd(II), Pt(II), and Ni(II) with chelation of the two Se atoms to the metal.[12,19] Surprisingly, though, the neutral Ni(II) complex of $[N(SP^iPr_2)_2]^-$ has a tetrahedral geometry.[13] The Q,Q′-chelation mode that uses both chalcogen donor atoms is well-represented.[8,10,12−16] A variety of other bonding motifs have been found with imidodiphosphinochalcogenido ligands, including multimetallic cluster compounds with bridging ligands.[17,20,21]

Scheme 1



$[N(QPR_2)_2]^-$

By far the focus of chemistry with the imidodiphosphinochalcogenido ligands has centered on late transition metals owing

---

(1) Churchill, M. R.; Cooke, J.; Fennessey, J. P.; Wormald, J. *Inorg. Chem.* **1971**, *10*, 1031−1035.
(2) Rossi, R.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1992**, 435−437.
(3) Rossi, R.; Marchi, A.; Marvelli, L.; Magon, L.; Peruzzini, M.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1993**, 723−729.
(4) Balakrishna, M. S.; Klein, R.; Uhlenbrock, S.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.* **1993**, *32*, 5676−5681.
(5) Haiduc, I.; Silvestru, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Polyhedron* **1993**, *12*, 69−75.
(6) Casas, J. S.; Castiñeiras, A.; Haiduc, I.; Sánchez, A.; Sordo, J.; Vázquez-López, E. M. *Polyhedron* **1994**, *13*, 2873−2879.
(7) Balakrishna, M. S.; Santarsiero, B. D.; Cavell, R. G. *Inorg. Chem.* **1994**, *33*, 3079−3084.
(8) Silvestru, C.; Rösler, R.; Haiduc, I.; Cea-Olivares, R.; Espinosa-Pérez, G. *Inorg. Chem.* **1995**, *34*, 3352−3354.
(9) Bhattacharyya, P.; Woollins, J. D. *Polyhedron* **1995**, *14*, 3367−3388.
(10) Bhattacharyya, P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2489−2495.
(11) Bhattacharyya, P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 3189−3193.
(12) Bhattacharyya, P.; Novosad, J.; Phillips, J.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 1607−1613.
(13) Cupertino, D.; Keyte, R.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Inorg. Chem.* **1996**, *35*, 2695−2697.
(14) Cea-Olivares, R.; Novosad, J.; Woollins, J. D.; Slawin, A. M. Z.; García-Montalvo, V.; Espinosa-Pérez, G.; García y García, P. *Chem. Commun.* **1996**, 519−520.
(15) Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1996**, 2893−2901.
(16) García-Montalvo, V.; Novosad, J.; Kilian, P.; Woollins, J. D.; Slawin, A. M. Z.; García y García, P.; López-Cardoso, M.; Espinosa-Pérez, G.; Cea-Olivares, R. *J. Chem. Soc., Dalton Trans.* **1997**, 1025−1029.
(17) Bhattacharyya, P.; Slawin, A. M. Z.; Smith, M. B. *J. Chem. Soc., Dalton Trans.* **1998**, 2467−2475.
(18) Muñoz-Hernández, M.-A.; Singer, A.; Atwood, D. A.; Cea-Olivares, R. *J. Organomet. Chem.* **1998**, *571*, 15−19.
(19) Papadimitriou, C.; Veltsistas, P.; Novosad, J.; Cea-Olivares, R.; Toscano, A.; Garcia y Garcia, P.; Lopez-Cardosa, M.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **1997**, *16*, 2727−2729.
(20) Slawin, A. M. Z.; Ward, J.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1994**, 421−422.
(21) Laguna, A.; Laguna, M.; Rojo, A.; Fraile, M. N. *J. Organomet. Chem.* **1986**, *315*, 269−276.

10.1021/ic990602n CCC: $18.00

to the stability of the resultant complexes. With $[N(SePR_2)_2]^-$, the main-group metals have only recently gained attention.[14,22,23] The main-group complexes $[Et_2Ga\{N(SePPh_2)_2\}]$ and $[R_2Al\{N(SePPh_2)_2\}]$ (R = Me, Et, ^tBu), examples of hard Lewis acidic metals coordinated to selenium centers, have been prepared.[18] In the former complex there is a distorted tetrahedral coordination about the Ga atom with *Se,Se′*-coordination from the ligand. Spectroscopic studies indicate that the latter complexes have very weak Al−Se interactions. Another relatively neglected group of hard Lewis acids are the yttrium and lanthanide elements (from here on termed rare-earth (Ln) elements collectively). Only a few examples exist of rare-earth imidodiphosphinochalcogenido complexes, namely, $[\{\eta^3\text{-}N(SePPh_2)_2\}\{\eta^2\text{-}N(SePPh_2)_2\}Sm(THF)_2]$, $[\{\eta^2\text{-}N(SPPh_2)_2\}_2Sm(THF)_2]$, $[\{\eta^2\text{-}N(SePPh_2)_2\}_2Sm(SePh)(THF)]$, and $[\{\eta^3\text{-}N(SePPh_2)_2\}_2Sm(SeMes)(THF)]$ (Mes = mesityl).[24] In the first compound, one Se ligand bonds η^3 and the other bonds η^2 to the Sm center. Furthermore, only recently have rare-earth to chalcogenide bonds been observed and structurally characterized.[25−39] Considerable work has evolved toward stabilizing those bonds with the use of bulky substituents on the rare-earth atom, the chalcogen atom, or both.[25,27,29,32−34,40] Note that whereas some of the more attractive molecular precursors for solid-state rare-earth oxides are metal β-diketonates,[41] useful precursors to solid-state rare-earth chalcogenides are very limited. Given the similarity of the imidodiphosphinochalcogenido ligand to the well-developed bidentate oxide ligands, its rare-earth complexes are possible candidates as precursors.

In this paper we report the synthesis and X-ray crystal structures of $Cp_2Y[\eta^3\text{-}N(QPPh_2)_2]$ (Q = S (**1**), Se (**2**)). These compounds represent rare examples of the coordination of the imidodiphosphinochalcogenido ligands to hard Lewis acidic metals. The η^3-ligation in compound **1** is the first example of such a bonding motif for $[N(SPPh_2)_2]^-$. Also, we report the ^1H, ^{31}P, ^{77}Se (for **2**), and ^{89}Y NMR spectroscopies of the complexes; these provide insight into the solution behavior of these molecules.

Experimental Section

General Procedures. All manipulations were carried out under strict exclusion of dioxygen and water with the use of standard Schlenk techniques.[42] Tetrahydrofuran (THF) was distilled from Na−benzophenone and bubbled with Ar for 10 min before use. Pentane was refluxed before distillation over P_2O_5, and Ar gas was bubbled through it for 5 min before use. Tris(cyclopentadienyl)yttrium was synthesized by a published procedure and stored in an Ar-filled glovebox before use.[43] $HN(QPPh_2)_2$ was synthesized from $HN(PPh_2)_2$ and elemental chalcogen in a manner similar to published procedures.[10,12] $KN(QPPh_2)_2$ was made from the corresponding free acid and KO^tBu in MeOH analogously to a literature procedure.[10] NMR data on CD_2Cl_2 solutions of **1**, **2**, and $HN(QPPh_2)_2$, and 10:1 DMF:CD_2Cl_2 solutions of $KN(QPPh_2)_2$ were recorded on either a Gemini 300 MHz spectrometer (^{31}P (for **1**) and ^1H with a 5 mm NMR probe) or a 400 MHz Varian Spectrometer (^{31}P and ^{77}Se with a 10 mm broad-band NMR probe, ^{89}Y with a 10 mm low-frequency probe) at room temperature. ^{31}P chemical shifts, in ppm, were recorded at 120.470 MHz for **1** and at 161.904 MHz for **2** and were referenced to an external standard of 85% H_3PO_4 (set to 0.0 ppm). ^{77}Se chemical shifts, in ppm, were recorded at 76.295 MHz and referenced to an external standard of a saturated solution of diphenyl diselenide in C_6D_6 (set to 460 ppm). ^{89}Y chemical shifts, in ppm, were recorded at 19.598 MHz and referenced to an external standard of 3M YCl_3 in D_2O. The ^{31}P NMR spectrum for **2** was collected on a 0.11 M solution of **2** in CD_2Cl_2 with the following parameters: 4605 transients; d1 = 0 s; pulse width = 10 μs. ^{31}P NMR parameters for **1** were similar to those for **2**, though done on a different machine. ^{77}Se NMR spectra for $HN(SePPh_2)_2$ and $KN(SePPh_2)_2$ were collected as follows: 100 transients; d1 = 1 s; pulse width = 20 μs; 0.1 M solutions (CD_2Cl_2 for the free acid, 10:1 CD_2Cl_2:DMF for the K^+ salt). ^{77}Se NMR collection parameters for **2**: 871 transients; d1 = 10 s; pulse width = 20 μs; 0.11 M solution of **2** in a 1:4 mixture of CD_2Cl_2/CH_2Cl_2. ^{89}Y NMR collection parameters for **1**: 3115 transients; d1 = 20 s; pulse width = 20 μs; 0.2 M solution of **1** in CD_2Cl_2. ^{89}Y NMR collection parameters for **2**: 2727 transients; d1= 20 s; pulse width = 20 μs; 0.2 M solution of **2** in CD_2Cl_2. Melting point determinations were performed with a Mel-Temp device on samples sealed in glass capillaries. Elemental analyses were performed by Oneida Research Services.

$(C_5H_5)_2Y[\eta^3\text{-}N(SPPh_2)_2]$, 1. A 1:1 molar ratio of white crystalline Cp_3Y (100 mg, 0.35 mmol) and white powdered $HN(SPPh_2)_2$ (158 mg, 0.35 mmol) was loaded in separate flasks in an Ar-filled glovebox. The flasks were removed from the box and attached to a Schlenk line where 10 mL of THF was added to each via syringe. The clear solution of the free acid was added via syringe to the clear solution of Cp_3Y and the resulting clear solution was stirred for 1 h. The volume of the THF solution was reduced to 10 mL, and 10 mL of pentane was added. While sitting overnight at −15 °C, the solution produced large clear colorless crystals of **1**. Mp: 269−271 °C. Yield: 117 mg (50%). Anal. Calcd for $C_{34}H_{30}NP_2S_2Y$: C, 61.17; H, 4.53; N, 2.10. Found: C, 61.05; H, 4.55; N, 1.72. ^1H NMR: 6.16 ppm (s, 10H), 7.38 ppm (m, 8H), 7.44 ppm (m, 12H). $^{31}P\{^1H\}$ NMR: 47.8 ppm (d, $^2J_{P-Y} = 4$ Hz). $^{89}Y\{^1H\}$ NMR: −169.5 ppm (t, $^2J_{Y-P} = 4$ Hz). No absorption is present in the UV/vis spectrum between 230 and 800 nm.

$(C_5H_5)_2Y[\eta^3\text{-}N(SePPh_2)_2]$, 2. The synthesis was similar to that of **1** and gave a clear colorless crystalline product. Mp: 250−252 °C. Yield: 64%. Anal. Calcd for $C_{34}H_{30}NP_2Se_2Y$: C, 53.64; H, 3.97; N, 1.84. Found: C, 53.09; H, 3.81; N, 1.43. ^1H NMR: 6.18 ppm (d, 10H, Cp, $^2J_{Y-H} = 0.5$ Hz), 7.25 ppm (m, 8H), 7.39 ppm (m, 4H), 7.53 ppm (m, 8H). $^{31}P\{^1H\}$ NMR: 41.03 ppm ($^2J_{P-P} = 66$ Hz, $^1J_{P-Se} = 604$ Hz, $^2J_{P-Y} = 4$ Hz). $^{77}Se\{^1H\}$ NMR: −126.8 ppm ($^1J_{Se-Y} = 12$ Hz). $^{89}Y\{^1H\}$ NMR: −152.6 ppm (t, $^2J_{Y-P} = 4$ Hz). No absorption is present in the UV/vis spectrum between 230 and 800 nm.

---

(22) Cea-Olivares, R.; Canseco-Melchor, G.; García-Montalvo, V.; Hernández-Ortega, S.; Novosad, J. *Eur. J. Inorg. Chem.* **1998**, 1573−1576.

(23) Cea-Olivares, R.; García-Montalvo, V.; Novosad, J.; Woollins, J. D.; Toscano, R. A.; Espinosa-Pérez, G. *Chem. Ber.* **1996**, *129*, 919−923.

(24) Geissinger, M.; Magull, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 755−761.

(25) Schumann, H.; Albrecht, I.; Gallagher, M.; Hahn, E.; Janiak, C.; Kolax, C.; Loebel, J.; Nickel, S.; Palamidis, E. *Polyhedron* **1988**, *7*, 2307−2315.

(26) Berg, D. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1988**, *7*, 1858−1863.

(27) Berardini, M.; Emge, T.; Brennan, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 8501−8502.

(28) Berardini, M.; Emge, T. J.; Brennan, J. G. *J. Chem. Soc., Chem. Commun.* **1993**, 1337−1338.

(29) Brewer, M.; Khasnis, D.; Buretea, M.; Berardini, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1994**, *33*, 2743−2747.

(30) Khasnis, D. V.; Brewer, M.; Lee, J.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1994**, *116*, 7129−7133.

(31) Berardini, M.; Emge, T.; Brennan, J. G. *J. Am. Chem. Soc.* **1994**, *116*, 6941−6942.

(32) Cary, D. R.; Arnold, J. *Inorg. Chem.* **1994**, *33*, 1791−1796.

(33) Cary, D. R.; Ball, G. E.; Arnold, J. *J. Am. Chem. Soc.* **1995**, *117*, 3492−3501.

(34) Lee, J.; Brewer, M.; Berardini, M.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 3215−3219.

(35) Berardini, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 5327−5334.

(36) Freedman, D.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1997**, *119*, 11112−11113.

(37) Melman, J. H.; Emge, T. J.; Brennan, J. G. *J. Chem. Soc., Chem. Commun.* **1997**, 2269−2270.

(38) Freedman, D.; Melman, J. H.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 4162−4163.

(39) Melman, J. H.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1999**, *38*, 2117−2122.

(40) Arnold, J. *Prog. Inorg. Chem.* **1995**, *43*, 353−417.

(41) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1995**, *19*, 727−750.

(42) Shriver, D. F.; Drezdon, M. A. *Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(43) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 6210.

Table 1. Crystal Data (−120 °C) and Structure Refinement for $(C_5H_5)_2Y[\eta^3\text{-}N(SPPh_2)_2]$ (**1**) and $(C_5H_5)_2Y[\eta^3\text{-}N(SePPh_2)_2]$ (**2**)

	1	**2**
chemical formula	$C_{34}H_{30}NP_2S_2Y$	$C_{34}H_{30}NP_2Se_2Y$
formula weight	667.56	761.36
a (Å)	9.685(5)	9.745(5)
b (Å)	12.176(6)	12.222(6)
c (Å)	13.978(7)	13.930(7)
α (deg)	87.382(9)	88.024(9)
β (deg)	87.358(9)	87.380(9)
γ (deg)	68.689(9)	69.137(9)
V, Å^3	1533.1(13)	1548.4(14)
d_{calcd} (g/cm^3)	1.446	1.633
space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
linear abs coeff (cm^{-1})	22	44
$R_1(F)^a$ ($F_o^2 > 2s(F_o^2)$)	0.0469	0.0563
$R_w(F_o^2)^b$(all data)	0.120	0.127

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

X-ray Crystallography. Clear thin square plates of **1** and **2** were isolated under oil in an N_2-filled crystal mounting box and suspended in a Nylon loop before being quickly frozen in a dry N_2 stream of a diffractometer for data collection. Data for both compounds were collected at −120 °C with a Bruker Smart CCD diffractometer with the use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Final unit cell dimensions were obtained from 8192 reflections tallied during data processing. Data collections in *ω* scan mode were performed with the program SMART.[44] Cell refinement, data reduction, and face-indexed numerical absorption corrections were applied with the use of the program SAINT.[44] The program SADABS was also applied to address incident beam anomalies (crystal decay, incident beam absorption, and different generator settings among frames) through the assignment of individual scale factors for each frame and the smoothing of them with a seven-point quadratic Savitsky−Golay filter.[44] The structures were solved by standard Patterson methods and refined by full-matrix least-squares methods.[45] The final models were restricted to anisotropic displacement parameters for all non-hydrogen atoms and were ultimately refined to final $R_1(F)$ values of 0.047 (**1**) and 0.056 (**2**) for those data having $F_o^2 > 2\sigma(F_o^2)$. Some hydrogen atoms were found in difference electron density maps but all were ultimately generated in calculated positions and constrained with the use of a riding model. The isotropic displacement parameter for a given hydrogen atom was set 20% larger than the atom to which it is attached. Crystallographic data are listed in Table 1 and selected bond distances and angles are listed in Table 2.

Results and Discussion

Syntheses. The reaction of a 1:1 stoichiometry of $HN(QPPh_2)_2$ with Cp_3Y in THF followed by concentration and dilution of the solution with pentane yields clear crystals of analytically pure compounds $Cp_2Y[N(SPPh_2)_2]$ (**1**) and $Cp_2Y[N(SePPh_2)_2]$ (**2**) as is outlined in reaction 1:

$$HN(QPPh_2)_2 + Cp_3Y \rightarrow Cp_2Y[\eta^3\text{-}N(QPPh_2)_2] + CpH \quad (1)$$

Isolated yields for the reaction were 50% and 64% for **1** and **2**, respectively. Whereas no color change is apparent, the progress of the reaction is evident owing to an increase in the solubility of the products relative to the starting material. The compounds are soluble in THF and CH_2Cl_2; they are unstable toward air and water but are stable under inert conditions and in air under oil for extended periods of time. Neither shows absorptions in the UV/vis spectrum above 230 nm. Crystals of **1** and **2** suitable for diffraction studies are easily grow from concentrated THF solutions diluted with pentane. Suitable crystals can also be obtained from cooled, concentrated CH_2Cl_2 solutions of the compounds.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(C_5H_5)_2Y[\eta^3\text{-}N(SPPh_2)_2]$ (**1**) and $(C_5H_5)_2Y[\eta^3\text{-}N(SePPh_2)_2]$ (**2**)

	1	**2**
Y(1)−Q(1)	2.9345(16)	3.0524(18)
Y(1)−Q(2)	2.9278(19)	3.0528(13)
Y(1)−N(1)	2.431(3)	2.449(5)
Y(1)−Cp(1)	2.394	2.392
Y(1)−Cp(2)	2.377	2.379
Y(1)−P(1)	3.3154(17)	3.397(2)
Y(1)−P(2)	3.3290(18)	3.378(2)
P(1)−N(1)	1.615(3)	1.632(5)
P(2)−N(1)	1.634(3)	1.633(5)
P(1)−Q(1)	1.9905(19)	2.1432(18)
P(2)−Q(2)	1.9845(18)	2.1406(19)
Q(1)−Y(1)−Q(2)	126.94(4)	129.54(3)
Cp(1)−Y(1)−Cp(2)	125.9	126.0
P(1)−N(1)−P(2)	142.9(2)	138.6(3)
Q(1)−P(1)−N(1)	104.99(14)	104.33(17)
Q(2)−P(2)−N(1)	104.66(14)	104.90(18)
Q(1)−Y(1)−N(1)	63.85(9)	64.96(11)
Q(2)−Y(1)−N(1)	64.04(8)	65.20(11)
C(11)−P(1)−C(17)	104.7(2)	107.0(3)
C(23)−P(2)−C(29)	107.3(2)	105.6(3)
Cp(1)−Y(1)−N(1)	125.9	124.0
Cp(2)−Y(1)−N(1)	109.0	110.0
Cp(1)−Y(1)−Q_{av}	114.6	115.3
Cp(2)−Y(1)−Q_{av}	119.5	118.7
Y(1)−P(1)−C(11)	133.01(15)	124.0(2)
Y(1)−P(1)−C(17)	121.25(16)	127.6(2)
Y(1)−P(2)−C(23)	125.12(17)	133.3(2)
Y(1)−P(2)−C(29)	126.07(18)	119.86(19)

[a] Cp(1) and Cp(2) are the centroids of atoms C(1) through C(5) and of atoms C(6) through C(10), respectively. Q = S in **1** and Se in **2**. Q_{av} is the midpoint of the line connecting the two Q atoms.

The protonolysis reaction is a general one for Cp_3Ln (Ln = Y or rare-earth element) compounds.[46−52] The route provides a clean way to make substituted Cp_2Ln compounds. The synthesis entails protonating and displacing a Cp ring on the Ln atom by an acid stronger than cyclopentadienene (HCp).[53] Other examples of protonolysis reactions for the synthesis of metal imidodiphosphinochalcogenido species are known. Trialkyl gallium and aluminum complexes are protonated with $HN(SePPh_2)_2$ to give the species $[Et_2Ga\{N(SePPh_2)_2\}]$ and $[R_2Al\{N(SePPh_2)_2\}]$ (R = Me, Et, ^{t}Bu).[18] Under conditions of excess ligand, these reactions stop at the monosubstituted species, as in the present work (see below). The ligands of the rare-earth complexes $La[N(SiMe_3)_2]_3$ and $Y[N(SiMe_3)_2]_3$ can be displaced with $HSeSi(SiMe_3)_3$ to form the species $La[SeSi(SiMe_3)_3]_3$ and

---

(44) SMART and SAINT-Plus Versions 5.101 Data Collection and Processing Software for the SMART System; Bruker Analytical X-Ray Instruments, Inc., Madison, WI, 1997.

(45) Sheldrick, G. M. SHELXTL PC Version 5.0 An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data. Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1994.

(46) Wu, Z.; Xu, Z.; You, X.; Zhou, X.; Xing, Y.; Jin, Z. *J. Chem. Soc., Chem. Commun.* **1993**, 1494−1495.

(47) Wu, Z.; Xu, Z.; You, X.; Zhou, X.; Jin, Z. *Polyhedron* **1992**, *11*, 2673−2678.

(48) Deacon, G. B.; Nickel, S.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *409*, C1−C4.

(49) Bielang, G.; Fischer, R. D. *Inorg. Chim. Acta* **1979**, *36*, L389-L390.

(50) Ye, Z.; Yu, Y.; Wang, S.; Jin, X. *J. Organomet. Chem.* **1993**, *448*, 91−93.

(51) Stehr, J.; Fischer, R. D. *J. Organomet. Chem.* **1993**, *459*, 79−86.

(52) Shi, L.; Ma, H.; Yu, Y.; Ye, Z. *J. Organomet. Chem.* **1988**, *339*, 277−282.

(53) Kanellakopulos, B.; Dornberger, E.; Billich, H. *J. Organomet. Chem.* **1974**, *76*, C42−C44.

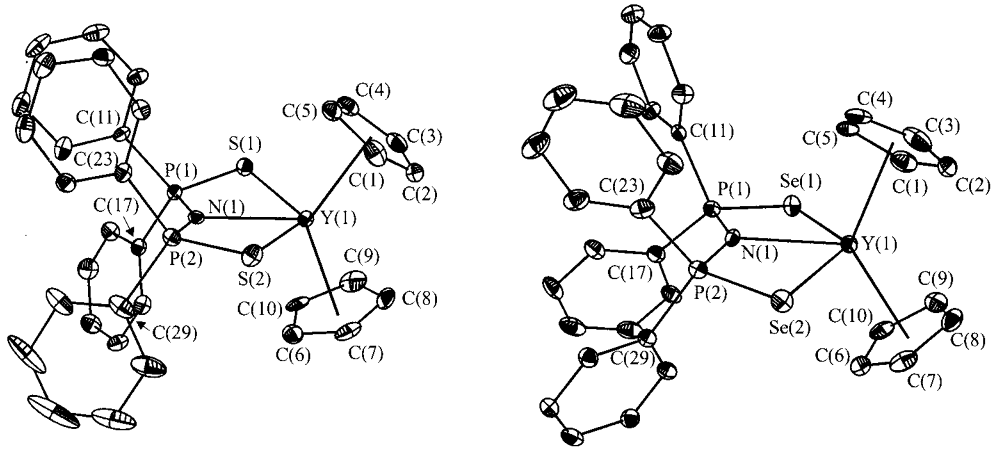


Figure 1. The structures of $Cp_2Y[\eta^3\text{-}N(SPPh_2)_2]$ (**1**) and $Cp_2Y[\eta^3\text{-}N(SePPh_2)_2]$ (**2**). Anisotropic displacement parameters are drawn at the 30% probability level. H atoms have been omitted for the sake of clarity.

$[Y\{SeSi(SiMe_3)_3\}_2\{\mu\text{-}SeSi(SiMe_3)_3\}]_2$ in good yields that are reduced by the high solubility of the end products.[33] Similarly, whereas NMR studies on the present compounds (see below) indicate full conversion to products **1** and **2**, isolated yields are substantially less.

Structures. Drawings of both molecules are shown in Figure 1. The structures are very similar, with each comprising an $[N(QPPh_2)_2]^-$ ligand coordinated η^3 through two Q atoms and an N atom to a Cp_2Y fragment. The molecules possess approximate 2-fold symmetry. Down the Y−N bond there are noticeable distortions in the intersecting Q_2P_2N and Cp_2Y planes. In **1**, the following deviations of the ligand in the YP_2 plane are seen: S(1) (−0.351 Å), S(2) (−0.057 Å), N(1) (0.063 Å). In **2**, the deviations in the YP_2 plane are as follows: Se(1) (−0.015 Å), Se(2) (0.372 Å), N(1) (−0.033 Å). In each, the Q atom with the larger deviation from the mean YP_2 plane is displaced toward the Cp ring having the larger Cp−Y(1)−N(1) angle. The Cp(1)−Y(1)−N(1) and Cp(2)−Y(1)−N(1) angles differ substantially, averaging about 125° vs about 110° in both compounds (Cp(1) is the centroid of atoms C(1) through C(5), and Cp(2) is the centroid of atoms C(6) through C(10); see Table 2). The $Cp\text{-}Y\text{-}Q_{av}$ angles (where Q_{av} is the midpoint of the line connecting the two Q atoms) though imply symmetrical bonding of the ligand to the Cp_2Y fragment (114.6° and 119.5° for **1** and 115.3° and 118.7° for **2**). Similarly, both the acetylacetonato and 1,1,1-trifluoroacetylacetonato ligands bond symmetrically between the Cp rings in $(C_5H_5)_2Yb(CH_3COCHCOCH_3)$[50] and $(C_5H_5)_2Yb(CH_3COCHCOCF_3)$.[52] Symmetrical bonding is also found between the Cp rings in the dimers $[(C_5H_5)_2Yb(\eta^1\text{-}OCH_2CH_2CH_3)]_2$[46] and $[(C_5H_5)_2Gd(\mu\text{-}\eta^2\text{-}ONCMe_2)]_2$.[54]

The Y−P−C angles are relatively consistent. Each face of the ligand (the face being defined as one of the sides of the YNP_2Q_2 planes) has two angles in the range 124.0(2)°−133.0(2)° and two in the range of 119.9(2)°−126.1(2)°. The largest angles alternate faces. The closest H···H contacts to the $(C_5H_5)^-$ rings are normal at 2.4 Å; in **2** these contacts are intermolecular, whereas in **1** they are intramolecular.

The bite angle (Q(1)−Y(1)−Q(2)) of the η^3-coordinated $[N(QPPh_2)_2]^-$ ligand is substantially larger than that of the η^2-coordinated ligand. For example, this angle is 126.94(4)° in **1**, 129.54(3)° in **2**, and 125.39(4)° in $[Sm\{\eta^2\text{-}N(SePPh_2)_2\{\eta^3\text{-}N(SePPh_2)_2(THF)_2]$,[24] the only other example of η^3-bonding, whereas representative bite angles in Q,Q′-coordinated complexes are 101.27(3)° in $[Pd(C_9H_{12}N)\{N(SePPh_2)_2\}]$,[17] 99.7(1)° in $[Pt(C_8H_{12}OMe)\{N(SPPh_2)_2\}]$,[17] and 92.51(4)° in $[Sm\{\eta^2\text{-}N(SPPh_2)_2\}_2(THF)_2]$.[24]

The Y−S distances (2.935(2) and 2.928(2) Å) in **1** are considerably longer than terminal Y−S distances (2.587(3) and 2.681(3) Å) and bridging Y−S distances (2.848(3) and 2.850(3) Å) in $[(Et_3CS)_2Y(\mu\text{-}SCEt_3)Py_2]_2$.[55] But the coordination numbers of Y differ in these compounds and a single negative charge is shared by three bonds in the present compound compared with one in the terminal and two in the bridging Y−S bonds in the example. Similarly, Y−Se distances in **2** (3.052(2) and 3.053(1) Å) are longer than the bridging Y−Se distance in $[(^tBuC_5H_5)_2Y(\mu\text{-}SePh)]_2$ (2.915(1) Å),[56] although there are very few Y−Se distances to be found in the literature.

The Y−N distances for **1** and **2** (2.431(3) and 2.449(5) Å, respectively) are longer than nominal Y−N single bond distances in negatively charged N-containing species, such as $Y[N(SiMe_3)_2]_3$[57] (2.224(6) Å) and $(C_6H_5CN)_2Y[N(SiMe_3)_2]_3$[57] (range 2.248(4)−2.257(4) Å) but are shorter than the Y−N bond distances where the N donors are neutral, for example 2.613(4) Å in $[HB(pz)_3]_2YCl(HPz)$ (Pz = pyrazole)[58] and 2.490(4) Å for the benzylnitrile−Y bond in $(C_6H_5CN)_2Y[N(SiMe_3)_2]_3$.[57]

NMR Studies. NMR spectroscopy has proved very useful for elucidating the nature of rare-earth chalcogenide species in solution. Such species are known to exhibit complex equilibria.[33] For example, in the synthesis of the Y− and La−selenide species cited above, the dimeric nature of the Y species was confirmed by multinuclear NMR studies. Although paramagnetism precludes NMR studies on many rare-earth compounds, the present Y species are diamagnetic, so high-resolution NMR spectroscopy involving at least four possible NMR active nuclei (^1H, ^{31}P, ^{77}Se (in **2**), and ^{89}Y) is feasible.

The NMR spectra of compounds **1** and **2** as well as the free acid and K^+ salts of the ligand are summarized in Table 3. ^{31}P NMR data for starting materials $HN(QPPh_2)$ (Q = S, Se) dissolved in CD_2Cl_2 were collected at room temperature to keep

---

(54) Wu, Z.; Zhou, X.; Zhang, W.; Xu, Z.; You, X.; Huang, X. *J. Chem. Soc., Chem. Commun.* **1994**, 813−814.

(55) Purdy, A. P.; Berry, A. D.; George, C. F. *Inorg. Chem.* **1997**, *36*, 3370−3375.

(56) Beletskaya, I. P.; Voskoboynikov, A. Z.; Shestakova, A. K.; Yanovsky, A. I.; Fukin, G. K.; Zacharov, L. N.; Struchkov, Y. T.; Schumann, H. *J. Organomet. Chem.* **1994**, *468*, 121−124.

(57) Westerhausen, M.; Hartmann, M.; Pfitzner, A.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 837−850.

(58) Reger, D. L.; Lindeman, J. A.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 3923−3929.

Table 3. Summary of Selected NMR Spectroscopy[a]

compound	solvent	^{31}P	^{77}Se	^{89}Y	$^{1}J_{\mathrm{P-Se}}$	$^{2}J_{\mathrm{P-P}}$	$^{2}J_{\mathrm{P-Y}}$
1	CD$_2$Cl$_2$	47.80		−152.9			4
2	CD$_2$Cl$_2$	41.03	−126.8	−169.5	604	66	4
HN(SPPh$_2$)$_2$	CD$_2$Cl$_2$	56.87					
HN(SePPh$_2$)$_2$	CD$_2$Cl$_2$	52.26	−162.8		790	25	
KN(SPPh$_2$)$_2$	DMF/CD$_2$Cl$_2$	37.10					
KN(SePPh$_2$)$_2$	DMF/CD$_2$Cl$_2$	28.52	−118.8		693	8	

[a] Chemical shifts are in ppm. Coupling constants are in Hz. See Experimental Section for additional parameters.

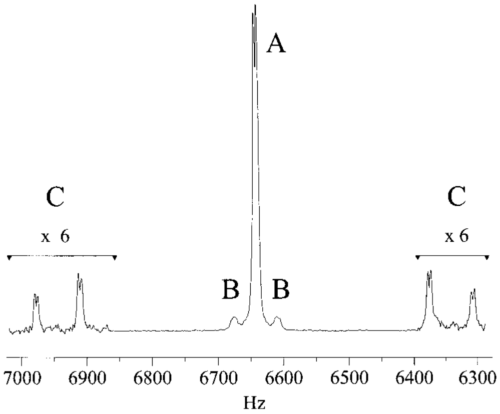


Figure 2. ^{31}P{^{1}H} NMR spectrum of **2**. The main peak (A, comprising approximately 85% of the intensity) is a doublet. The inner satellites constitute a doublet of doublets (B, approximately 7.5% of the intensity) and the outer satellites a doublet of doublets of doublets (C, approximately 7.5% of the intensity).

consistent collection parameters throughout this study (see Experimental Section for further details). ^{77}Se NMR data for the starting materials have not been previously published. All NMR spectra collected indicate that on the NMR time scale the molecules possess 2-fold symmetry in solution, in contrast to their structures in the solid state. Furthermore, the molecules retain their Y−Q bonds in solution. The ^{31}P spectra show a shift down in frequency from 56.87 and 52.26 ppm in the S and Se starting materials, respectively, to 47.8 (**1**) and 41.03 ppm (**2**). This shift moves the resonances closer to the ^{31}P resonances in the K$^+$ salt of the ligand (Table 3). The same trend is seen in the ^{31}P NMR spectra of other metal(III) complexes of the ligand: Sb[N(SePPh$_2$)$_2$]$_3$ (25.4 ppm),[23] Bi[N(SePPh$_2$)$_2$]$_3$ (27.3 ppm),[23] In[N(SePPh$_2$)$_2$]$_3$ (28.5 ppm),[23] and [RuCl{N(SePPh$_2$)$_2$}(η^6-*p*-MeC$_6$H$_4$Pr^i)] (29.0 ppm).[17] The ligands in these species are Se, Se′-coordinated. The splitting of the ^{31}P NMR resonances in **1** and **2** is readily discernible. In **1**, the main peak is coupled through two bonds to the ^{89}Y nucleus ($I = {}^1/_2$, 100% abundance) ($^{2}J_{\mathrm{P-Y}} = 4$ Hz) representative of an A$_2$X spin system (where A = ^{31}P and X = ^{89}Y). In **2** (Figure 2), the main peak is similarly split into a doublet from two-bond coupling to the ^{89}Y nucleus ("A" in Figure 2, $^{2}J_{\mathrm{P-Y}} = 4$ Hz). Additionally, the coupling arising from one spin-active ^{77}Se nucleus ($I = 1/2$, 7.8% abundance) being present gives satellites from the AA′MX spin system in which the ^{31}P atoms (A, A′) are magnetically inequivalent. With two positions that the ^{77}Se nucleus (M) can occupy, the probability of at least one ^{77}Se nucleus being present is 0.156 (2 × 0.078) and the probability that two be present is 0.006 (0.078 × 0.078); hence, the probability that only one be present is 0.156 − 0.006 = 0.150. The spectrum arising from two spin active Se atoms being present is too weak to be observed, and therefore, each of the outside satellite peaks ("C" in Figure 2) should integrate to 7.5% of the total intensity. Indeed, each integrates to 7−8%. These arise from the ^{31}P nucleus adjacent to the ^{77}Se atom whose signal is split by the other ^{31}P ($^{2}J_{\mathrm{P-P}} = 66$ Hz) and the ^{77}Se ($^{1}J_{\mathrm{P-Se}} = 604$ Hz) nuclei. The $^{2}J_{\mathrm{P-P}}$ coupling is also seen in the inner satellites surrounding the main peak ("B" in Figure 2, which integrate to approximately 7.5% of the total intensity). These arise from the ^{31}P that is three bonds from the ^{77}Se nucleus and therefore whose signal is split by the other ^{31}P nucleus ($^{2}J_{\mathrm{P-P}} = 66$ Hz). Both of these assignments assume that the P atoms have similar chemical shifts and that the $^{3}J_{\mathrm{P-Se}}$ coupling is negligible. All satellites are partially split into doublets owing to the $^{2}J_{\mathrm{P-Y}}$ coupling ($^{2}J_{\mathrm{P-Y}} = 4$ Hz), though this is not well-resolved in the innermost satellites. A decrease in the $^{1}J_{\mathrm{P-Se}}$ coupling constant compared with that of the free acid and K$^+$ salts of the ligand indicates a reduction of the P−Se bond order. The large $^{2}J_{\mathrm{P-P}}$ coupling relative to other compounds and to the starting material probably results from the near planarity of the ligand, which allows efficient electron delocalization. The ^{31}P NMR splitting pattern is further corroborated by the ^{77}Se NMR spectrum (Figure 3). A doublet of doublets at −126.8 ppm confirms the P−Se splitting found in the ^{31}P spectrum and further gives a one-bond Y−Se splitting of 12 Hz.

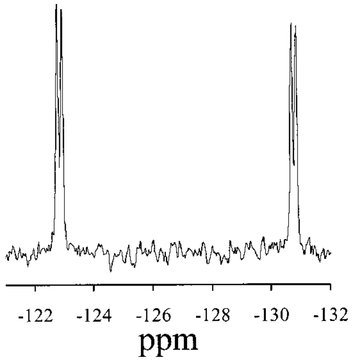


Figure 3. ^{77}Se{^{1}H} NMR spectrum of **2**. A doublet of doublets arises from $^{1}J_{\mathrm{Se-P}}$ (604 Hz) and $^{1}J_{\mathrm{Se-Y}}$ (12 Hz) coupling.

The ^{77}Se NMR shift of this ligand has only been investigated in one other molecule, [Sn{N(SePPh$_2$)$_2$-*Se,Se*′}$_2$] (9.8 ppm).[14] We collected the ^{77}Se NMR spectra for the free acid (−162.8 ppm) and K$^+$ salt (−118.8 ppm) of the ligand to provide references. The ^{77}Se NMR resonances in **2** are shifted substantially to higher frequencies from the free acid and are closer to that of the K$^+$ salt. The shift in the ^{77}Se NMR spectrum is similar to that for [Y{SeSi(SiMe$_3$)$_3$}$_2${μ-SeSi(SiMe$_3$)$_3$}]$_2$, which shows resonances at −120 and −131 ppm[33] for the two inequivalent Se atoms.

^{89}Y NMR spectroscopy was performed on **1** and **2** to confirm the $^{2}J_{\mathrm{P-Y}}$ coupling of 4 Hz in each compound. The Y−P coupling is much less than the coupling obtained from spectra of compounds containing ligands with direct Y−P bonds, such as YCl[N(SiMe$_2$CH$_2$PMe$_2$)$_2$]$_2$ ($^{1}J_{\mathrm{Y-P}} = 52$ Hz),[59] but close to those obtained from the spectra of Y(BHT)$_3$(OP^{n}Bu$_3$)$_2$ (BHT = O-2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$; $^{2}J_{\mathrm{Y-P}} = 14.2$ Hz)[60] and Y(OSiPh$_3$)$_3$(OP^{n}Bu$_3$)$_2$ ($^{2}J_{\mathrm{Y-P}} = 8.7$ Hz),[60] where the P atoms are two bonds away from the Y centers. A single triplet was found at −169.5 ppm for **1** and −152.9 ppm for **2** relative to 3 M YCl$_3$ in D$_2$O. The shifts are expected, given the shielding power of the Cp rings. For instance, in the series YCl$_3$, (CH$_3$C$_5$H$_4$)$_2$YCl(THF), and (CH$_3$C$_5$H$_4$)$_3$Y(THF), the Y atoms are progressively shielded

---

(59) Fryzuk, M. D.; Haddad, T. S. *J. Am. Chem. Soc.* **1988**, *110*, 8263−8265.

(60) Coan, P. S.; Hubert-Pfalzgraf, L. G.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 1262−1267.

(61) Evans, W. J.; Meadows, J. H.; Kostka, A. G.; Closs, G. L. *Organometallics* **1985**, *4*, 324−326.

as (substituted) Cp rings replace the Cl ligands (0, −102, and −371 ppm, respectively).[61] The NMR peak shifts in **1** and **2** are governed by the Cp rings, as the ^{89}Y NMR resonance of the compound $[Y\{SeSi(SiMe_3)_3\}_2\{\mu\text{-}SeSi(SiMe_3)_3\}]_2$ is very deshielded at 995 ppm.[33]

The addition of more than 1 equiv of the ligands to the Cp_3Y starting material produces only compounds **1** and **2** and excess ligand, as ^{31}P NMR studies of reaction mixtures show only the resonances for compounds **1** and **2** and the free ligand. Moreover, THF dissolved in a CD_2Cl_2 solution of complexes **1** and **2** does not coordinate to the Y atoms, as there is no appreciable shift in frequency of the THF ^1H NMR resonances relative to free THF in solution.

In a preliminary extension of the present chemistry to other rare-earth elements, it appears that the smaller elements may only accommodate η^2-bonding from the ligand.

Acknowledgment. This research was kindly supported by the National Science Foundation, Grant CHE-9819385.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of $Cp_2Y[\eta^3\text{-}N(SPPh_2)_2]$ (**1**) and $Cp_2Y[\eta^3\text{-}N(SePPh_2)_2]$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

IC990602N