Inorg. Chem. **2006**, *45*, 8820–8822

Inorganic Chemistry

Communication

Novel Metalloreagent $Cp(CO)_2FeP(Se)(OR)_2$ Produced from P–Se Bond Cleavage in the Thermal Reaction of $[CpFe(CO)_2]_2$ with Phosphor-1,1-diselenolates

C. W. Liu,*,† Jem-Min Chen,† Bidyut Kumar Santra,† Sung-Yin Wen,† Ben-Jie Liaw,† and Ju-Chun Wang‡

Department of Chemistry, National Dong Hwa University, Hualien 974, Taiwan, and Department of Chemistry, Soochow University, Taipei 111, Taiwan

Received August 14, 2006

The reaction of $[CpFe(CO)_2]_2$ with $NH_4Se_2P(OR)_2$ yields a novel reagent $Cp(CO)_2FeP(Se)(OR)_2$, which has demonstrated coordination properties at the Se center to form heterometallic clusters as well as reactivity at the Se site toward C-based electrophiles.

Organophosphorus compounds such as phosphor-1,1-diselenolates [$(RO)_2PSe_2^-$, dsep] have shown coordination ability via Se donor atoms, as well as Se transfer activity, in their reactions with metal ions such as Cu^I, Ag^I, and Zn^{II}, leading to the formation of Se-centered clusters, namely, $[M_8(\mu_8\text{-}Se)\{Se_2P(O^iPr)_2\}_6]$ (M = Cu, Ag), $[M_{11}(\mu_9\text{-}Se)(\mu_3\text{-}X)_3\{Se_2P(O^iPr)_2\}_6]$ (M = Cu, Ag; X = Br, I), $[Ag_{10}(\mu_{10}\text{-}Se)\{Se_2P(OEt)_2\}_8]$, and $[Zn(\mu_4\text{-}Se)\{Se_2P(OPr)_2\}_6]$.[1] The cleavage of P−Se bonds of diselenophosphate ligands obviously occurs during their reactions with salts of these metals. In all of the above-mentioned clusters, the origin of the central μ_n-Se moiety (n = 4, 8, 9, and 10) is the dsep ligand itself, although the precise mechanism of Se transfer at the centers of cubanes or other polyhedra is not yet well-understood. In contrast, the related organophosphorus compounds containing P−Se bonds, such as diselenophosphinates ($R_2PSe_2^-$),[2a] diselenophosphonates [$R(OR)PSe_2^-$],[2d] and triselenophosphonates ($RPSe_3^{2-}$),[3] have exhibited neither the P−Se cleavage activity nor the formation of similar clusters.[4] This shows that the lability of the P−Se bonds of the dsep ligands is probably due to the electromeric effect of the alkoxyl groups, which places these ligands in unique positions vis-à-vis other ligands to coordinate as well as undergo P−Se bond cleavage.

In the Se-transfer reactions forming clusters as discussed above,[1] the cleavage of the P−Se bond of dsep is believed to generate the $(RO)_2PSe$ moiety, which could not be identified in these reactions. In our pursuit to identify the $(RO)_2PSe$ moiety, it was envisaged that Fp dimers, $Cp_2Fe_2(CO)_4$, well-known to generate iron carbonyl radicals[5] either thermally or photolytically might entrap the $(RO)_2PSe$ moiety from [$(RO)_2PSe_2^-$] and lead to the formation of $Cp(CO)_2FeP(Se)(OR)_2$ **1**. The Fp dimer $Cp_2Fe_2(CO)_4$ has the propensity to cleave even stronger P−C, C−H, C−O, and P−O bonds of organophosphorus compounds such as bis(diphenylphosphino)methane[6] and tetraethyl diphosphite.[7] Another reason to pursue the synthesis of compound **1** was the fact that, surprisingly, there is no report to date of its formation, even though O and S analogues of **1**, namely, $Cp(CO)_2FeP(E)(OR)_2$ (E = O, S), have been known for decades.[8,9] It may be noted that dsep ligands have been known for almost 40 years,[10] but their coordination chemistry remained ignored because of their sensitivity to air until cluster chemistry was initiated in 1998 by Liu et al. using ammonium salts of

---

* To whom correspondence should be addressed. E-mail: chenwei@mail.ndhu.edu.tw. Fax: (+886) 3-863-3570.

† National Dong Hwa University.

‡ Soochow University.

(1) (a) Liu, C. W.; Chen, H.-C.; Wang, J.-C.; Keng, T.-C. *Chem. Commun.* **1998**, 1831. (b) Liu, C. W.; Hung, C.-M.; Wang, J.-C.; Keng, T.-C. *J. Chem. Soc., Dalton Trans.* **2002**, 3482. (c) Liu, C. W.; Hung, C.-M.; Santra, B. K.; Chu, Y.-H.; Lin, Z. *Inorg. Chem.* **2004**, *43*, 4306. (d) Liu, C. W.; Shang, I.-J.; Wang, J.-C.; Keng, T.-C. *Chem. Commun.* **1999**, 995. (e) Liu, C. W.; Shang, I.-J.; Hung, C.-M.; Wang, J.-C.; Keng, T.-C. *J. Chem. Soc., Dalton Trans.* **2002**, 1974. (f) Liu, C. W.; Shang, I.-J.; Fu, R.-J.; Liaw, B.-J.; Wang, J.-C.; Chang, I.-J. *Inorg. Chem.* **2006**, *45*, 1974. (g) Santra, B. K.; Hung, C.-M.; Liaw, B.-J.; Wang, J.-C.; Liu, C. W. *Inorg. Chem.* **2004**, *43*, 7570.

(2) (a) Davies, R. P.; Francis, C. V.; Jurd, A. P. S.; Martinelli, M. G.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2004**, *43*, 4802. (b) Annan, T. A.; Kumar, R.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1991**, 11. (c) Pilkington, M. J.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Polyhedron* **1991**, *10*, 2641. (d) Gray, I. P.; Slawin, A. M. Z.; Woollins, J. D. *Dalton Trans.* **2005**, 2188.

(3) (a) Davies, R. P.; Martinelli, M. G. *Inorg. Chem.* **2002**, *41*, 348. (b) Parkin, I. P.; Pilkington, M. J.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Polyhedron* **1990**, *9*, 987.

(4) Lobana, T. S.; Wang, J.-C.; Liu, C. W. *Coord. Chem. Rev.* DOI: 10.1016/j.ccr.2006.05.010.

(5) (a) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (b) Bitterwolf, T. E. *Coord. Chem. Rev.* **2000**, *206*−*207*, 419.

(6) Alvarez, C. M.; Galan, B.; Garica, M. E.; Riera, V.; Ruiz, M. A.; Vaissermann, J. *Organometallics* **2003**, *22*, 5504.

(7) Alvarez, C. M.; Galan, B.; Garica, M. E.; Riera, V.; Ruiz, M. A.; Bois, C. *Organometallics* **2003**, *22*, 3039.

(8) (a) Nakazawa, H.; Morimasa, K.; Kushi, Y.; Yoneda, H. *Organometallics* **1988**, *7*, 458. (b) Haines, R. J.; Du Preez, A. L.; Marais, I. L. *J. Organomet. Chem.* **197**1, *28*, 405.

(9) (a) Nakazawa, H.; Ichimura, S.; Nishihara, Y.; Miyoshi, K.; Nakashima, S.; Sakai, H. *Organometallics* **1998**, *17*, 5061. (b) Piraino, P.; Faraone, F.; Aversa, M. C. *J. Chem. Soc., Dalton Trans.* **1976**, 610.

10.1021/ic061538u CCC: $33.50

diselenophosphates.[1] These salts are easier to handle than the previously known alkali-metal salts.[10] Furthermore, the related compounds $Cp(CO)_2FeP(E)R_2$ (E = S, Se; R = CF_3, Ph) have been known since 1973.[11]

In this Communication, we report the synthesis and structure of the metalloreagent **1**. It is prepared easily. We have studied its reactivity toward C-based electrophiles as well as its coordination ability toward metal ions, which generate polymetallic complexes with the Fp [$=Cp(CO)_2Fe$] fragment acting as a flag at the terminal position. We note that while there are reports of reactivity at the E center of the P=E moiety of $Cp(CO)_2FeP(O)(OR)_2$[8] or $Cp(CO)_2FeP(E)R_2$ (E = S, Se; R = CF_3, Ph)[11] toward protonation or alkylation, there is no reported coordination chemistry involving E donor atoms.[12]

The reaction of the Fp dimer $Cp_2Fe_2(CO)_4$ (0.81 g, 2.30 mmol), with diisopropyl diselenophosphate (1.12 g, 3.35 mmol) in refluxing toluene at 110 °C for 4 h, yields compounds of composition $Cp(CO)_2FeP(Se)(O^iPr)_2$ (**1**; 0.58 g, 48% yield), characterized by analytical data, NMR, IR, and X-ray crystallography.[13,14] The ^{31}P NMR spectrum of **1** exhibits one signal with a pair of satellites due to $^{31}P-^{77}Se$ coupling (J_{P-Se} = 712.9 Hz), and the ^{77}Se NMR spectrum shows a doublet due to $^{77}Se-^{31}P$ coupling (J_{Se-P} = 713.3 Hz). This coupling constant suggests that the title compound contains a P−Se partial double bond. Figure 1 displays the structure of compound **1** in which the Fe center is bound to the P atom of the selenophosphito moiety. The geometry around the P center is distorted tetrahedral, with Se−P−Fe being the largest. The Se−P bond distance of 2.128 Å is indicative of a partial double bond. Therefore, the observed selenophosphito fragment in **1** clearly suggests that P−Se bond cleavage occurs in the thermal reaction of $[CpFe(CO)_2]_2$ with phosphor-1,1-diselenolates. Very few reports focus on the P−Se bond activation. Complexes of the type *trans*-$M(PhSe)[P(O)(OPh)_2][PEt_3]_2$ (M = Pd, Pt), which were produced from the reaction of $PhSeP(O)(OEt)_2$ with $M(PEt_3)_3$ and likely to proceed via the oxidative addition of a P−Se bond to Pd^0 and Pt^0 complexes, are two notable examples.[15]

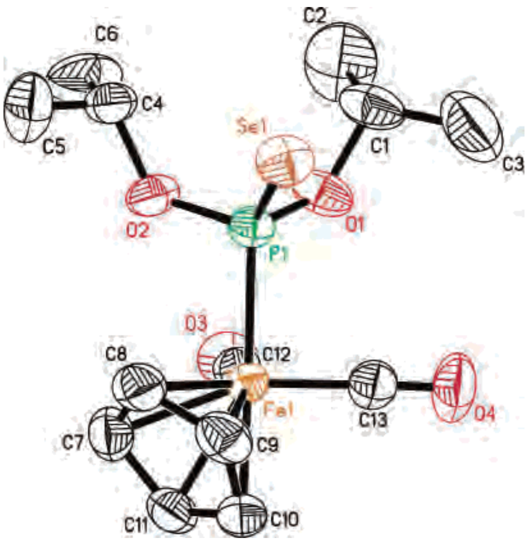
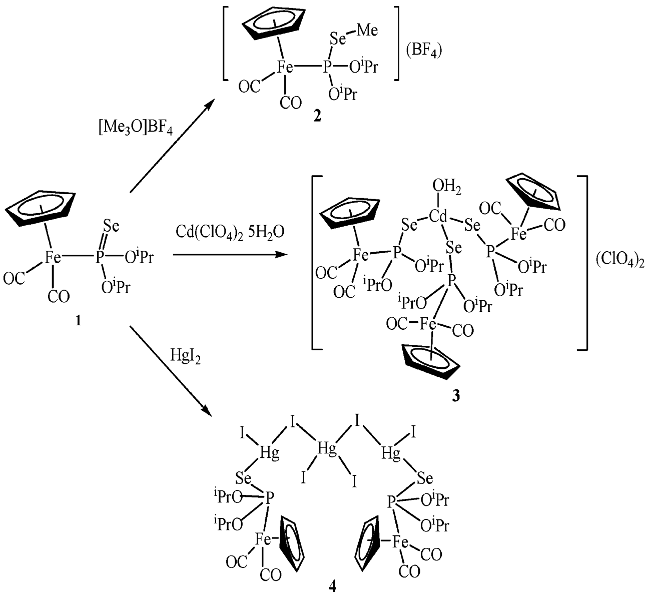


Figure 1. Structure of compound **1**. Only one of the two independent molecules is depicted (H atoms are omitted). Selected bond lengths (Å) and angles (deg): Fe1−P1 2.215(1), Se1−P1 2.128(1), O−P1 1.600(3), 1.593(3); Se1−P1−Fe1 117.8(1), O−P1−Fe1 104.2(1), 106.6(1), O−P1−Se1 111.7(1), 110.8(1), O1−P1−O2 104.8(2).

Scheme 1 shows the reactions of **1** with the C-based electrophile, $(Me_3O)BF_4$, and the metal salt such as Cd^{II} and

Scheme 1



---

(10) (a) Kudchadker, M. V.; Zingaro, R. A.; Irgolic, K. J. *Can. J. Chem.* **1968**, *46*, 1415. (b) Krishnan, V.; Zingaro, R. A. *Inorg. Chem.* **1969**, *8*, 2337.

(11) (a) Dobbie, R. C.; Mason, P. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1124. (b) Dobbie, R. C.; Hopkinson, M. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1290.

(12) Unlike Kläui's anionic, tripodal ligand, $[CpCo\{P(O)(OEt)_2\}_3]^-$, which has been used as metalloligands through the O atoms, the metalloreagent of **1** is the neutral one.

(13) Spectroscopic data for **1**. Elem anal. Calcd for $C_{13}H_{19}FeO_4PSe$: C, 38.55; H, 4.73. Found: C, 39.17; H, 4.90. ^1H NMR ($CDCl_3$): δ 1.30 (12H, t, $^3J_{H-H} + ^4J_{H-P}$ = 6 Hz, CH_3), 4.90 (7H, m, CH + Cp). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 165.7 (P, s, $P(O^iPr)_2$, J_{P-Se} = 712.9 Hz). ^{13}C NMR ($CDCl_3$): δ 211.4 (d, $^2J_{P-C}$ = 30 Hz, CO), 87.9 (Cp), 71.2 (d, $^2J_{P-C}$ = 15 Hz, OCH), 23.8 (CH_3). ^{77}Se NMR ($CDCl_3$): δ 199.6 (d, $^1J_{P-Se}$ = 713.3 Hz). IR (CH_2Cl_2, ν(CO), cm^{-1}): 2039 and 1991. Spectroscopic data for **2**. Elem anal. Calcd for $C_{14}H_{22}BF_4FeO_4PSe\cdot0.5H_2O$: C, 32.59; H, 4.49. Found: C, 32.43; H, 4.39. ^1H NMR (acetone-d_6): δ 1.42 (12H, d, CH_3), 2.50 (3H, d, $^3J_{P-H}$ = 12.1 Hz, $SeCH_3$), 4.92 (2H, m, OCH), 5.72 (5H, s, Cp). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 183.2 (P, s, $P(O^iPr)_2$, J_{P-Se} = 425.6 Hz). ^{77}Se NMR ($CDCl_3$): δ 311.2 (d, J_{P-Se} = 420.2 Hz). IR (KBr, ν(CO), cm^{-1}): 2056 and 2012. Spectroscopic data for **3**. Elem anal. Calcd for $C_{39}H_{59}CdCl_2Fe_3O_{21}P_3Se_3$: C, 30.33; H, 3.85. Found: C, 29.62; H, 4.03. ^1H NMR (acetone-d_6): δ 1.42 (36H, d, CH_3), 4.93 (6H, m, OCH−), 5.5 (15H, s, Cp). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 176.2 (3P, s, J_{P-Se} = 600 Hz). ^{13}C NMR (acetone-d_6): δ 210.2 (CO), 88.9 (Cp), 75.1 (OCH), 23.5 (CH_3). IR (KBr, ν, cm^{-1}): 3444 (H_2O), 2043 and 1993 (CO), 1095 (ClO_4). Spectroscopic data for **4**. Elem anal. Calcd for $C_{26}H_{38}Hg_3I_6Fe_2P_2O_8Se_2$: C, 14.37; H, 1.76. Found: C, 14.39; H, 1.85. ^1H NMR (DMSO-d_6): δ 1.28 (24H, d, CH_3), 4.79 (4H, m, OCH−), 5.48 (10H, s, Cp). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 183.2 (2P, s, J_{P-Se} = 549.9 Hz, $^2J_{P-Hg}$ = 57.3 Hz). ^{77}Se NMR (DMSO-d_6): δ 271.2 (d, J_{P-Se} = 556.3 Hz). IR (KBr, ν(CO), cm^{-1}): 2052 and 2011.

(14) Crystal structure data for **1**: $C_{13}H_{19}FeO_4PSe$, M_r = 405.06, orthorhombic, *Pbca*, $a = 8.613(1)$ Å, $b = 27.093(1)$ Å, $c = 29.486(1)$ Å, $V = 6880.2(4)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.564$ Mg m^{-3}, μ(Mo Kα) = 3.093 mm^{-1}, R1 = 0.0425, wR2 = 0.0856 [$I > 2\sigma(I)$]. Crystal structure data for **3**: $C_{39}H_{59}CdCl_2Fe_3O_{21}P_3Se_3$, M_r = 1544.50, monoclinic, $P2_1/c$, $a = 16.192(4)$ Å, $b = 14.729(3)$ Å, $c = 25.366(6)$ Å, $\beta = 95.59(1)°$, $V = 6021(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.704$ Mg m^{-3}, μ(Mo Kα) = 3.105 mm^{-1}, R1 = 0.0444, wR2 = 0.1078 [$I > 2\sigma(I)$]. Crystal structure data for **4**: $C_{26}H_{38}Hg_3I_6Fe_2P_2O_8Se_2\cdot PMeOH$, M_r = 2205.34, tetragonal, *P*4(2)/*nbc*, $a = 20.5872(9)$ Å, $c = 26.0086(17)$ Å, $V = 11023.3(10)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.658$ Mg m^{-3}, μ(Mo Kα) = 13.617 mm^{-1}, R1 = 0.0264, wR2 = 0.0706 [$I > 2\sigma(I)$].

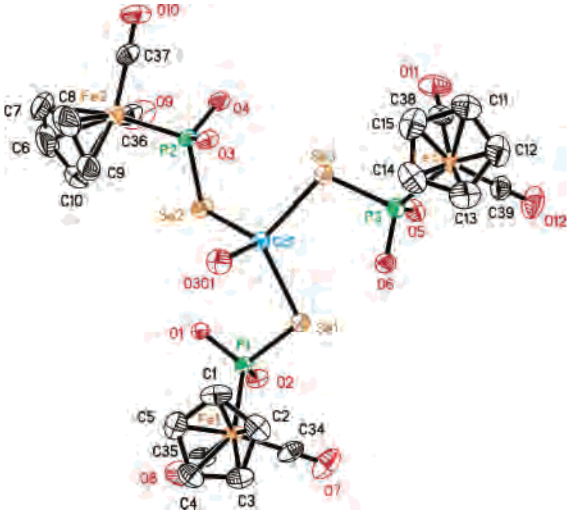


Figure 2. Structure of cation **3** with isopropyl groups omitted for clarity. Selected bond lengths (Å) and angles (deg): Cd1−Se 2.590(1)−2.603(1), Cd1−O301 2.307(4), Se−P (ave) 2.173(2), Fe−P (ave) 2.205(2); Se−Cd1−Se 110.69(3)−118.11(3), Se−Cd1−O301 98.89(12)−110.31(12), Cd1−Se−P (ave) 104.45(4), Se−P−Fe (ave) 112.0(1).

HgI_2 in methanol or acetone solvents forming Se-methylated compound **2** and heterometallic clusters **3** and **4**. Each successfully used **1** as the metalloligand. All of the compounds are well characterized.[13] The IR spectra reveal the characteristic peaks for two CO groups in the vicinity of 2000 cm^{-1} in each case. ^{31}P NMR spectra reveal a shift in the signal from δ 165.7 ppm in **1** ($J_{P-Se} = 712.9$ Hz) to δ 176.2−183.2 ppm in compounds **2**−**4** (δ, ppm; J_{P-Se}, Hz: 183.2, 425.6, **2**; 176.2, 600.0, **3**; 183.2, 549.9, **4**). Further, with Se being the site of coordination or alkylation, its ^{77}Se NMR spectrum is significantly affected. For example, the signal at δ 199.6 ppm ($J_{P-Se} = 713.3$ Hz) in **1** shifts to low field at δ 311.2 ppm ($J_{P-Se} = 420.2$ Hz) in **2** and at δ 271.2 ppm ($J_{P-Se}= 556.3$ Hz) in **4**. The ^{31}P NMR spectra reveal that the reduction in the P−Se coupling constant occurs in the order **2** > **4** > **3**. Thus, methylation at Se and binding to Hg affect the environment at Se to the largest extent in this series of compounds.

Figures 2 and 3 depict the structures of cations **3** as well as of nonionic compound **4**. The structural feature for **3** is that the Cd atom is surrounded trigonally by three Se atoms and the fourth coordination site is occupied by a H_2O molecule. Thus, the coordination geometry around Cd in **4** is distorted, or flattened tetrahedral. The Cd−Se bond distances range from 2.589(1) to 2.602(1) Å. The Hg_3 cluster **4** has each terminal Hg atom in an extremely distorted trigonal geometry and slightly distorted tetrahedral for the central Hg atom. Whereas the coordination sphere of the terminal Hg atoms is occupied by two iodo groups and one Se atom from the $Cp(CO)_2FeP(Se)(OR)_2$ unit, the central Hg atom is tetracoordinated by four iodo ligands. Interestingly, the cluster **4** exhibits a close $\pi\cdots\pi$ contact between two Cp rings, and the close rapport with two Cp rings (3.555 Å) may be one of the factors for the observed severe distortion revealed in the terminal Hg centers. Furthermore, the Se−P−Fe angle contracts from 117.8° in **1** to ~112°, after coordination to a metal center.

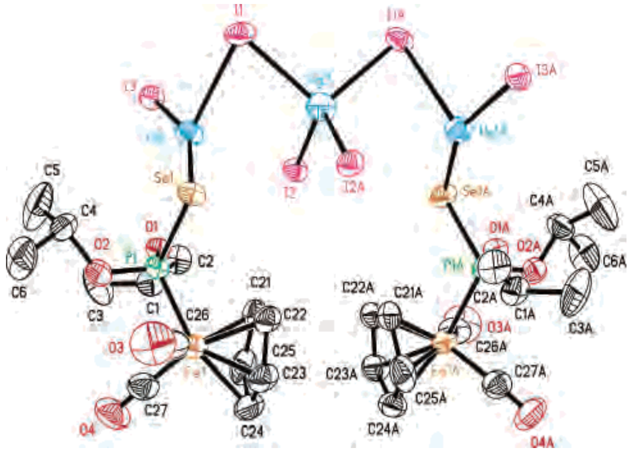


Figure 3. Structure of compound **4** with H atoms omitted. Selected bond lengths (Å) and angles (deg): Hg1−Se1 2.486(1), Hg1−I3 2.612(1), Hg1−I1 3.087(1), Hg2−I1 2.812(1), Hg2−I2 2.762(1), Se1−P1 2.208(2), Fe1−P1 2.185(2); Se1−Hg1−I3 153.72(3), Se1−Hg1−I1 93.00(3), I1−Hg1−I3 107.45(2), I2A−Hg2−I2 116.23(3), I2−Hg2−I1 106.49(2), I2−Hg2−I1A 110.67(2), I1A−Hg2−I1 105.87(3), Hg2−I1−Hg1 79.84(2), Hg1−Se1−P1 98.25(6), Se1−P1−Fe1 112.57(10).

Thus, $Cp(CO)_2FeP(Se)(OR)_2$ **1**, which can be considered as a dialkoxyselenophosphido (or dialkylselenophosphito) derivative of $Cp(CO)_2Fe$, is realized for the first time obtained via a simple preparative method.[16] Compounds similar to **1** and **2** with replacement of R by Et and Pr, as well as the utilization of **1** as the metalloligand to generate heterometallic clusters with group 11 metals, also have been prepared. They will be reported soon.

Acknowledgment. This research is supported by a grant (NSC-95-2119-M-259-001) from the National Science Council of Taiwan.

Supporting Information Available: Crystallographic data of **1**, **3**, and **4** in CIF format and ^1H NMR spectra of **2** and **3** in PDF format. This material is available free of charge via the Internet at http://pub.acs.org.

IC061538U

---

(15) Han, L.-B.; Choi, N.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 7000.

(16) One of the reviewers suggested characterizing species other than the $SeP(OR)_2$ moiety existing in this reaction. Whether the FpSe species might float around will be discussed in the subsequent full article.