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Tricarbonyl[(1−5-η)-pentadienyl]manganese: A Source of Benzeneselenolatomanganese Derivatives of Diverse Nuclearity

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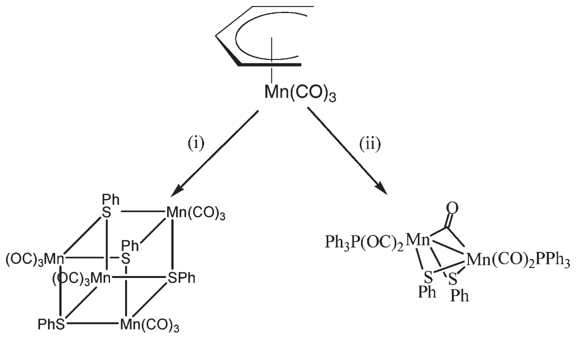
Summary: Reaction of tricarbonyl[*(1−5-η)-pentadienyl*]*manganese with benzeneselenol in the presence of bis*(*diphenylphosphino*)*ethane afforded a mononuclear* (*carbonyl*)(*phosphine*)-*manganese compound with the benzeneselenolato coordinated in a terminal fashion. A dinuclear compound with two bridging selenolato ligands and a bridging carbonyl was obtained when the organometallic precursor was made to react with benzeneselenol in the presence of triphenylphosphine. Direct reaction of tricarbonyl*[*(1−5-η)-pentadienyl*]*manganese with benzeneselenol gave the heterocubane* [*Mn*(μ_3-*SePh*)(*CO*)$_3$]$_4$.

Transition metal pentadienyl complexes have gained in interest during the last two decades. The rich structural, synthetic, and reaction chemistry of the pentadienyl complexes stem from the bonding capabilities of the pentadienyl ligand. As far as the reaction chemistry is concerned, nucleophilic attack on pentadienyl complexes has been extensively explored.[1] The range of pentadienyl complexes and attacking nucleophiles is wide according to their nature: (a) anionic nucleophile−cationic pentadienyl complex;[2] (b) neutral nucleophile−cationic pentadienyl complex;[3] (c) anionic nucleophile−neutral pentadienyl complex;[4] and (d) both nucleophile and pentadienyl complex neutral.[5] Reaction chemistry studies of neutral pentadienyl complexes toward neutral species have received reduced attention.

Scheme 1



(i) PhSH, Δ, 24% yield; (ii) PPh_3, PhSH, Δ, 74% yield

We have undertaken a systematic study on the reactivity of the complex tricarbonyl[(1−5-η)-pentadienyl]manganese, [Mn(η^5-C_5H_7)(CO)$_3$] (**1**), toward neutral nucleophiles.[6] One reaction path that has attracted our interest is the extrusion of the pentadienyl ligand promoted by Lewis bases. Mercaptans react with [Mn(η^5-C_5H_7)(CO)$_3$] (**1**) to afford thiolate heterocubane species;[7] when there are phosphine ligands in the reaction medium, dinuclear manganese complexes can be formed by one-pot synthesis[8] (see Scheme 1).

The relative strength of a Lewis base in the reaction medium will determine the reaction mechanism and/or type of product obtained. In order to broaden the scope of this synthetic approach, we have put our efforts into the synthesis of selenium analogues of alkylthiolatecarbonylmanganese complexes.[9] We report herein our results.

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[1] (a) Stahl, L.; Ernst, R. D. *Adv. Organomet. Chem.* **2008**, *55*, 137. (b) Ernst, R. D. *Comments Inorg. Chem.* **1999**, *21*, 285. (c) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255. (d) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125.

[2] See for example: (a) Chaudury, S. Donaldson, W. A. *J. Am. Chem. Soc.* **2006**, *128*, 5984, and references therein. (b) Yeh, M.-C. P.; Sun, M.-L.; Lin *Tetrahedron Lett.* **1991**, *32*, 113. (c) Bleeke, J. R.; Wittenbrink, R. J.; Clayton, T. W., Jr.; Chiang, M. Y. *J. Am. Chem. Soc.* **1990**, *112*, 6539. (d) McDaniel, K. F.; Kracker, L. R., II; Thamburaj, P. K. *Tetrahedron Lett.* **1990**, *31*, 2373. (e) Donaldson, W. A.; Ramaswamy, M. *Tetrahedron Lett.* **1989**, *30*, 1339. (f) Bleeke, J. R.; Rauscher, J. J. *J. Am. Chem. Soc.* **1989**, *111*, 8972. (g) Williams, G. M.; Rudisill, D. E. *Inorg. Chem.* **1989**, *28*, 797. (h) Bleeke, J. R.; Rauscher, J. J. *J. Am. Chem. Soc.* **1989**, *111*, 8972.

[3] See for example: (a) Hafner, A.; Bieri, J. H.; Prewo, R.; von Philipsborn, W.; Salzer, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 713. (b) McArdle, P.; Sherlock, H. *J. Chem. Soc., Chem. Commun.* **1976**, 537.

[4] See: Roell, B. J., Jr.; McDaniell, K. F. *J. Am. Chem. Soc.* **1990**, *114*, 9004.

[5] For some examples refer to: (a) Wilson, A. M.; West, F. G.; Arif, A. M.; Ernst, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 8490. (b) Hyla-Kryspin, I.; Waldman, T. E.; Melendez, E.; Trakarnpruk, W.; Arif, A. M.; Ziegler, M. L.; Ernst, R. D.; Gleiter, R. *Organometallics* **1995**, *14*, 5030. (c) Tomaszewski, R.; Lam, K.-Ch.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1999**, *18*, 4174. (d) Lin, W.-J.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1991**, *10*, 2519. (e) Bleeke, J. R Peng, W.-J. *Organometallics* **1986**, *5*, 635, and refs 6−8 of the present paper.

[6] (a) Zúñiga-Villarreal, N.; Paz-Sandoval, M. A.; Joseph-Nathan, P.; Esquivel, O. *Organometallics* **1991**, *10*, 2616. (b) Paz-Sandoval, M. A.; Juárez-Saavedra, P.; Zúñiga-Villarreal, N.; Rosales-Hoz, M. J.; Joseph-Nathan, P.; Ernst, R. D.; Arif, A. M. *Organometallics* **1992**, *11*, 2467. (c) Paz-Sandoval, M. A.; Sánchez-Coyotzi, R.; Zúñiga-Villarreal, N.; Ernst, R. D.; Arif, A. M. *Organometallics* **1995**, *14*, 1044.

[7] Reyes-Lezama, M.; Toscano, R. A; Zúñiga-Villarreal, N. *J. Organomet. Chem.* **1996**, *517*, 19.

[8] Reyes-Lezama, M.; Höpfl, H.; Zúñiga-Villarreal, N. *J. Organomet. Chem.* **2008**, *693*, 987.

[9] Common carbonylmanganese starting materials for organoselenolato complexes are [$Mn_2(CO)_{10}$], [NaMn(CO)$_5$], and [MnX(CO)$_5$] (X = halogen). As far as selenium starting materials are concerned, it is common practice to use deprotonated organoselenols, RSeSeR, or elemental selenium to incorporate them into carbonylmanganese moieties. Sweigart, D. A.; Reingold, J. A., Son, S. U. In *COMC III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, 2007; Vol. *5*.

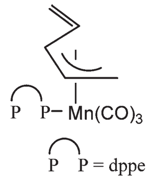
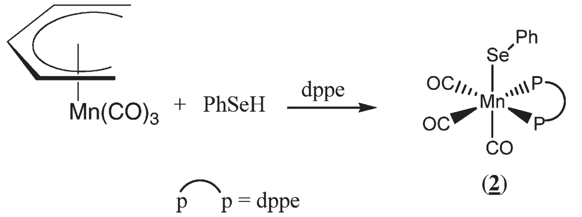


Figure 1. Proposed intermediate for generation of **2**.

Results and Discussion

Synthesis of Complexes [Mn(CO)$_3$(SePh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)κ^2-*P*,*P'*] (2), [Mn$_2$(CO)$_4$(μ-CO)(μ-SePh)$_2$(PPh$_3$)$_2$] (3), and [Mn(μ_3-SePh)(CO)$_3$]$_4$ (4). Mononuclear Complex [Mn(CO)$_3$(SePh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)κ^2-*P*,*P'*] (2). Complex **2** was obtained in 2.5 h in 87% yield by reaction of **1** with benzeneselenol in the presence of 1,2-bis(diphenylphosphino)ethane (dppe), in a 1:1:1 molar ratio, as shown in eq 1.



(1)

Complex **2** is a yellow-orange solid that melts at 120 °C with decomposition. In the solid state it is stable at low temperature (ca. −5 °C) for months in an atmosphere of argon. Decomposition to manganese oxide and Ph$_2$Se$_2$, among other unidentified products, occurs in solution within 3 h at room temperature in air. **2** is sparingly soluble in hexane and soluble in chlorinated solvents. It is noteworthy that **2** contains a terminal benzeneselenolate, since it is well-known that alkyl- and arylselenolates tend to form metal–selenium bridges (μ_2 and μ_3) with group 7 carbonyls. Terminal selenolate coordination is attributed to stabilization by dppe chelation. The presence of *trans*-piperylene (observed by proton NMR) in the present reaction leads us to suggest that an η^3-intermediate (see Figure 1) could be involved. Since it has already been shown that tricarbonyl[(1−5-η)-pentadienyl]manganese undergoes carbonyl substitution via an associative mechanism through an η^3-intermediate, which could be isolated,[10] we carried out the reaction of dppe with **1** in order to synthesize the intermediate shown in Figure 1; instead, we obtained a complex mixture of species that could not be characterized.

We suggest that the reaction time (2.5 h) is dependent on the dppe nucleophilicity in view of the fact that when aryl and alkyl mercaptans are made to react with **1** in the presence of dppe, similar reaction times are observed.[8]

Crystallization of complex **2** from a mixture of dichloromethane/hexane at low temperature afforded suitable crystals for an X-ray analysis. The ORTEP diagram is shown in Figure 2.

The geometry around the manganese atom is distorted octahedral. The Mn–C carbonyl distances are equal as are the Mn–P(1) and Mn–P(2) distances within experimental error. The selenium atom environment is best accounted for by an sp^3 hybridization with two free lone pairs.

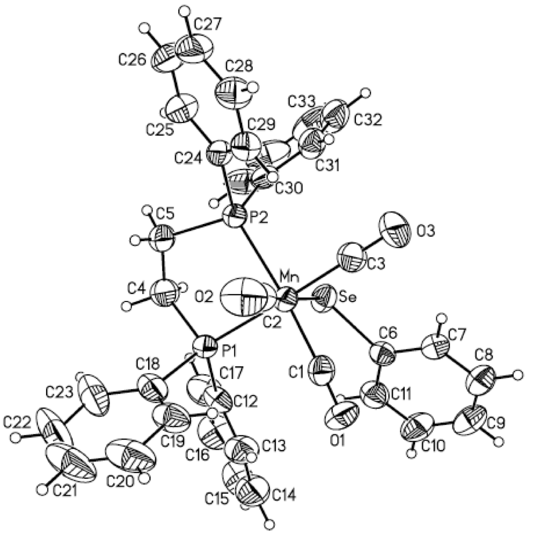
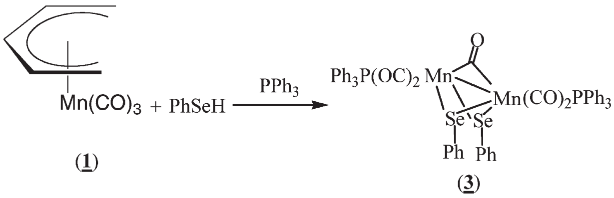


Figure 2. Molecular structure of **2** including labeling scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [deg]: Mn–Se 2.5136(8), Mn–P(1) 2.3243(13), Mn–P(2) 2.3173(1), Mn–C(1) 1.823(5), Mn–C(2) 1.776(5), Mn–C(3) 1.794(6); C(1)–Mn–P(2) 174.4(2), C(2)–Mn–Se 176.8(2), C(3)–Mn–P(1) 170.0(2), Mn–Se–C(6) 108.7(1).

Dinuclear Complex [Mn$_2$(CO)$_4$(μ-CO)(μ-SePh)$_2$(PPh$_3$)$_2$] (3). The presence of the triphenylphosphine in the reaction medium of **1** with benzeneselenol, eq 2, resulted in the formation of dinuclear complex **3**.



(2)

Complex **3** is a deep purple solid whose melting point is 115−117 °C. In the solid state it is stable at low temperature (ca. −5 °C) for months in argon atmosphere. Decomposition occurs in solution within 3 h at room temperature in air. **3** is soluble in chlorinated solvents.

The yield of **3** was 51% (based on **1**) and the reaction time was 8 h. The best stoichiometry was 1:1:2 (**1**:PPh$_3$:benzeneselenol, respectively) since when benzeneselenol was 1 equiv in excess (1:1:3), a shorter reaction time (4 h) and a lower yield (18%) were observed. This decrease in yield can be accounted for by formation of PhSeSePh.

We have reasons to believe that complex **3**, [Mn$_2$(CO)$_4$(μ-CO)(μ-SePh)$_2$(PPh$_3$)$_2$], has already been reported in the late 1960s.[11] At that time the molecular formula [Ph$_3$PMn(CO)$_3$(μ-SePh)]$_2$ was proposed supported by IR spectroscopy (CHCl$_3$: 1988m, 1949s, 1906s; no bridging carbonyl wavenumber was reported). The IR spectrum of **3** in the ν(CO) region showed the bands 1983vs, 1950vs, 1908s, 1794w in chloroform. The last band corresponds to a (μ-CO), which was substantiated by X-ray analysis (see below).

The reaction chemistry of benzeneselenol toward **1** in the presence of triphenylphosphine turned out to be similar to that of mercaptans.[8] It is well known that arylselenols are

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[10] Paz-Sandoval, M. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026.

[11] Abel, E. W.; Atkins, A. M.; Crosse, B. C., Hutson, G. V. *J. Chem Soc. A* **1968**, 687.

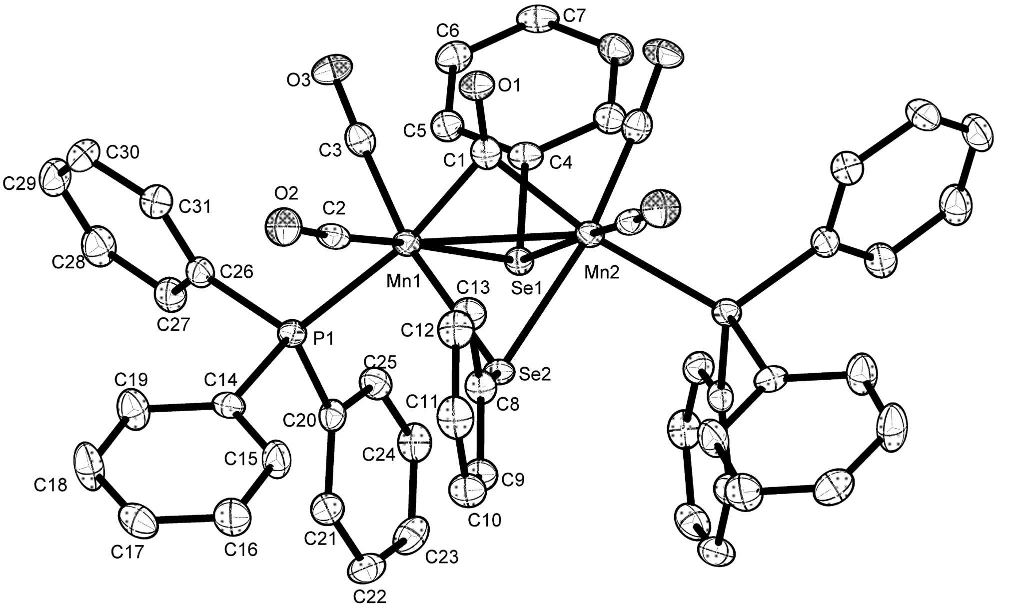


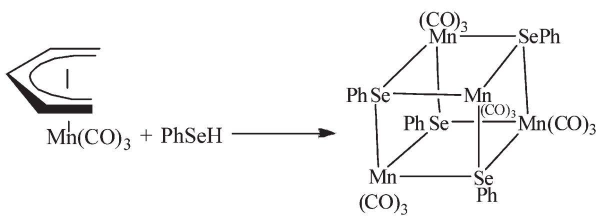
Figure 3. Molecular structure of **3** including atom-numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [deg]: Mn(1)−Mn(2) 2.6952(7), Mn(1)−C(1) 2.023(3), Mn(1)−P(1) 2.3457(6), Mn(1)−Se(1) 2.4310(4), C(1)−O(1) 1.159(4); Mn(1)−Se(1)−Mn(2) 67.33(2), Mn(1)−C(1)−Mn(2) 83.6(1), C(2)−Mn(1)−P(1) 86.11(7), P(1)−Mn(1)−C(1) 169.11(7), C(2)−Mn(1)−Se(1) 173.38(7), C(3)−Mn(1)−Se(2) 169.08(7).

better nucleophiles than arylthiols.[12] In the present case the reaction time for **3** (8 h) was longer than that reported for the sulfur analogue [$Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}SPh)_2(PPh_3)_2$] (40 min).[8] We suggest that Pearson's "soft−hard" acid−base considerations have to be taken into account to explain this reactivity: Complex **1** better matches the "hardness" of phenyl mercaptan than that of benzeneselenol.

Crystallization of complex **3** from a mixture of dichloromethane/hexane at low temperature afforded suitable crystals for X-ray studies. The ORTEP diagram is shown in Figure 3.

The geometry around the manganese center is distorted octahedral. The bridging selenolates and the bridging carbonyl are symmetrical. The carbon atom of the bridging carbonyl lies *trans* to the phosphine ligands, while the selenium atoms of the selenolate ligands are *trans* to carbonyl groups. The phenyl rings on the selenium atoms present an *exo-syn* conformation and orient themselves perpendicularly to each other.

Tetranuclear Complex [$Mn(\mu_3\text{-}SePh)(CO)_3]_4$ (4). Reaction of complex **1** with benzeneselenol afforded heterocubane **4** as shown in eq 3.

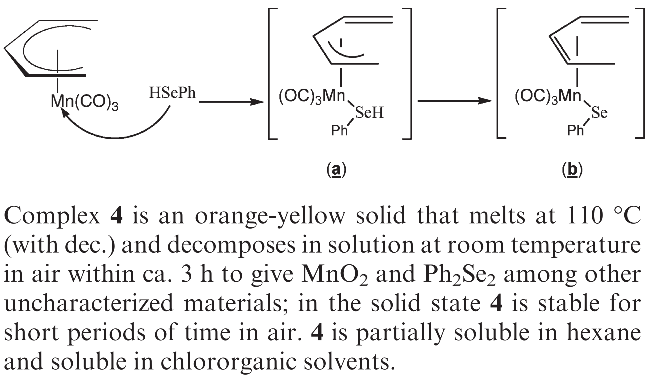


(3)

(1) (4)

A 63% yield of **4** was obtained with an equimolar ratio and a reaction time of 5 h under cyclohexane reflux. Longer reaction times and/or excess of benzeneselenol led to lower reaction yields and formation of unidentified products.

Scheme 2. Proposed Intermediates for the Formation of 4



Complex **4** is an orange-yellow solid that melts at 110 °C (with dec.) and decomposes in solution at room temperature in air within ca. 3 h to give MnO_2 and Ph_2Se_2 among other uncharacterized materials; in the solid state **4** is stable for short periods of time in air. **4** is partially soluble in hexane and soluble in chlororganic solvents.

The formation of tetranuclear complex **4** can be explained by PhSeH coordination to the Mn center followed by saturation of the pentadienyl ligand to *cis*-piperylene, Scheme 2. Reaction intermediate [$Mn(\eta^4\text{-}C_5H_8)(SePh)(CO)_3$], **b** in Scheme 2, functions as a sort of [$-Mn(SePh)(CO)_3$] transfer agent, which in the absence of Lewis bases assembles with other like moieties (being a Lewis base itself) to afford tetranuclear complex **4**. It is well known that metal-dienyl complexes generally seem to be much more susceptible to protonation[13] than the metallocenes, for which very acidic conditions are required; however, in our hands **1** did not react toward C_6F_5SH[14] (more acidic than C_6H_5SeH) at cyclohexane reflux temperature. This leads us to propose that formation of **4** could go through intermediate **a**, which, upon migration of a hydrogen atom, would afford **b**. Despite the fact that we have not detected any manganese hydride by

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(12) Peach, M. E. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; John Wiley & Sons: Bristol, 1974; Part 2.

(13) (a) Newbound, T. D.; Stahl, L.; Ziegler, M. L.; Ernst, R. D. *Organometallics* **1990**, *9*, 2962. (b) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1260. (c) Werner, R; Werner, H. *Chem. Ber.* **1984**, *117*, 161. (d) Derome, A. E.; Green, M. L. H.; OHare, D. *J. Chem. Soc., Dalton Trans.* **1986**, 343. (e) Bleeke, J. R.; Moore, D. A. *Inorg. Chem.* **1986**, *25*, 3522. (f) Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417.

(14) Unpublished results.

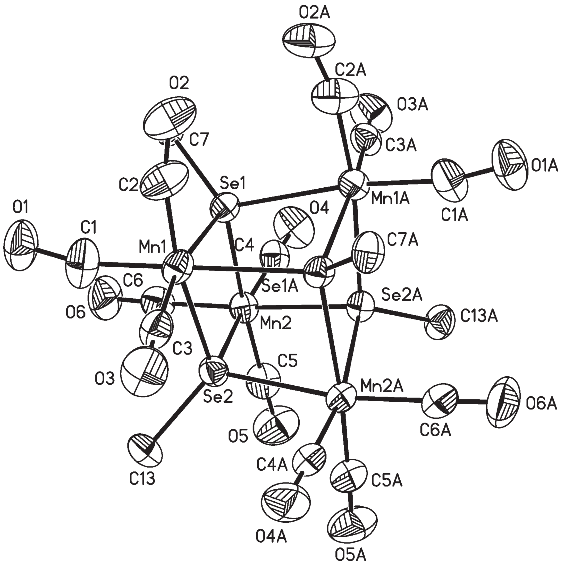

Figure 4. Molecular structure of **4** including atom-numbering scheme (ORTEP drawing with 50% probability ellipsoids; only *ipso*-phenyl carbons shown for the sake of clarity). Selected bond lengths [Å] and angles [deg]: Mn(1)−Se(1A) 2.4890(7), Mn(1)−Se(1) 2.5038(6), Mn(1)−Se(2) 2.5046(7), Mn(1)−(CO)$_{av}$ 1.800(4); C(1)−Mn(1)−Se(1A) 171.6(1), C(2)−Mn(1)−Se(2) 171.4(2), C(3)−Mn(1)−Se(1) 168.4(1).

^{1}H NMR, an oxidative addition of the Se−H bond to the metal center and then hydrogen migration to the pentadienyl ligand cannot be ruled out.

Complex **4** has been obtained by photolysis of [$Mn_2(CO)_{10}$] and PhSeSePh for 12 h at room temperature in 35−40% yield;[15] its characterization was achieved spectroscopically. No crystal structure studies have ever been reported of selenium heterocubanes to the best of our knowledge. A mixture of dichloromethane/hexane at low temperature afforded crystals of **4** for an X-ray analysis. The ORTEP diagram is shown in Figure 4. Complex **4** is a distorted heterocubane where the benzeneselenolato ligands function in the capacity of μ_3-bridges.

Conclusions

Simple, one-pot syntheses were devised for the preparation of mono-, di-, and tetranuclear carbonylmanganese complexes using [Mn(η^5-C_5H_7)(CO)$_3$] and the corresponding phosphines and benzeneselenol. The relative nucleophilicity of both the benzeneselenol and the phosphine ligand determines the reaction times. The incorporation of both phosphine and selenium ligands in one reaction step is possible due to the occupancy of the vacant sites that the pentadienyl ligand leaves behind after its extrusion. One important limitation of the present synthesis method for aryl- or alkylselenium manganese carbonyl complexes is the availability of organoselenium compounds. However, this reaction type allows for the coordination of a great deal of ligands that have proven to have little or no coordination abilities at all to bind a carbonylmanganese moiety; studies thereof are underway.

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Supporting Information Available: Crystallographic information files, textual summary of data collection, refinement data, experimental procedures, and IR spectra of complexes **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org

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(15) Jaitner, P. *J. Organomet. Chem.* **1981**, *210*, 353.

(16) Seyferth, D.; Goldman, W. E.; Pornet, J. *J. Organomet. Chem.* **1981**, *208*, 189.