498 *Organometallics* **1998,** *17,* 498−500

Heterocumulene Metathesis of $Pb[N(SiMe_3)_2]_2$. High-Yield Syntheses of the Heteroleptic Dimer $\{Pb[N(SiMe_3)_2(\mu\text{-}OSiMe_3)\}_2$ and the Novel Lead(II) Oxo Cluster $Pb_7(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu\text{-}OSiMe_3)_{10}$

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Received November 21, 1997

*Summary: Metathesis of $Pb[N(SiMe_3)_2]_2$ (**1**) with 1 and 2 equiv of Bu^{t}NCO has been used to prepare, in high yields, the novel lead(II) trimethylsilanolato compounds $\{Pb[N(SiMe_3)_2(\mu\text{-}OSiMe_3)\}_2$ (**2**) and $Pb_7(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu\text{-}OSiMe_3)_{10}$ (**4**), respectively. Although $[Pb(OSiMe_3)_2]_n$ (**3**) could not be obtained through this process, these results serve to further elucidate the extents and limitations of heterocumulene metathesis as a synthetic tool.*

Lead(II) dialkoxides and bis(triorganosilanolates), $[Pb(OR)_2]_n$ (R = alkyl and SiR′$_3$, respectively), hold great promise as molecular precursors to lead-containing metal oxide materials.[1,2] On the other hand, these compounds are notoriously difficult to prepare by standard methods, as trace impurities are known to catalyze their conversion to lead(II) oxo clusters of the general formulas $Pb_4(\mu_4\text{-}O)(\mu\text{-}OR)_6$ and $Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_4$.[1a,c,f,3,4] Perhaps for this reason, $[Pb(OSiR'_3)_2]_n$ derivatives remain virtually unknown as a class of compound.[4−6] Recently, we have been exploring the use of heterocumulene metathesis of metal triorganosilylamides as a new synthetic tool that can be used to prepare, under very mild conditions, metal triorganosilanolates of either marginal stability and/or of novel structure according to $M{-}N(SiR_3)_2 + O{=}C{=}X \rightarrow M\text{-}OSiR_3 + R_3SiN{=}C{=}X$ (X = O, NR).[7,8] Accordingly, it was of interest to determine if this methodology could be extended to the synthesis of lead(II) triorganosilanolates as well. Herein, we now report that metathesis of $Pb[N(SiMe_3)_2]_2$ (**1**)[9] with *tert*-butyl isocyanate, Bu^{t}NCO, can be used to selectively prepare, in high yield, the remarkably stable heteroleptic dimer $\{Pb[N(SiMe_3)_2](\mu\text{-}OSiMe_3)\}_2$ (**2**) to our knowledge, the first example of a fully characterized mixed amido alkoxy (siloxy) lead(II) compound. Further, although $[Pb(OSiMe_3)_2]_n$ (**3**)[6] could not be obtained through this process, we document that this compound is most likely transiently generated from **1** by heterocumulene metathesis but that it undergoes conversion, via $(Me_3Si)_2O$ eliminations, to provide in near-quantitative yield $Pb_7(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu\text{-}OSiMe_3)_{10}$ (**4**), a new group 14 oxo cluster class of unprecedented molecular structure.

As Scheme 1 shows, reaction of **1** with 1 equiv of Bu^{t}NCO produced compound **2** in a near-quantitative yield as determined by ^{1}H NMR spectroscopy, and on a preparative scale, **2** could be isolated in 67% yield after recrystallization from a toluene/pentane solvent mixture at −40 °C.[10] Like the known tin(II) dimer $\{Sn[N(SiMe_3)_2](\mu\text{-}OBu^t)\}_2$ (**5**),[11] spectroscopic data are consistent with **2** possessing a dimeric structure in solution. Thus, by variable-temperature ^{1}H NMR (400 MHz, toluene-d_8), the singlet resonance at 0.26 ppm observed for the $-N(SiMe_3)_2$ group in the fast exchange limit at 25 °C broadened and decreased in intensity as the temperature was lowered until the coalescence temperature of −90 °C for exchange between two magnetically inequivalent $-SiMe_3$ environments that arise from hin-

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(10) To a solution of 0.914 g (1.84 mmol) of **1** in 10 mL of pentane was added a solution of 0.203 g (2.05 mmol) of Bu^{t}NCO in 5 mL of pentane. The reaction mixture was stirred for 18 h, whereupon a yellow solution was produced. The volatiles were then removed *in vacuo* to yield a white solid material which was then recrystallized from a toluene/pentane mixture at −40 °C to yield 0.566 g (67% yield) of pure **2**. Data for **2**: ^{1}H NMR (400 MHz, 25 °C, toluene-d_8) δ 0.11 (s, 18 H), 0.26 (s, 36 H); ^{207}Pb{^{1}H} NMR (83.8 MHz, 25 °C, benzene-d_6, relative to $PbEt_4$) δ 2442.8. Anal. Calcd for $C_9H_{27}NOPbSi_3$: C, 23.67; H, 5.96; N, 3.07. Found: C, 23.16; H, 5.77; N, 2.77.

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S0276-7333(97)01027-3 CCC: $15.00
Publication on Web 01/22/1998

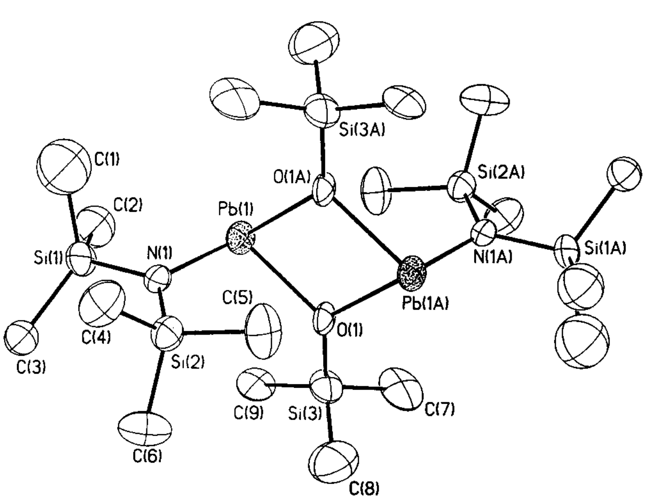
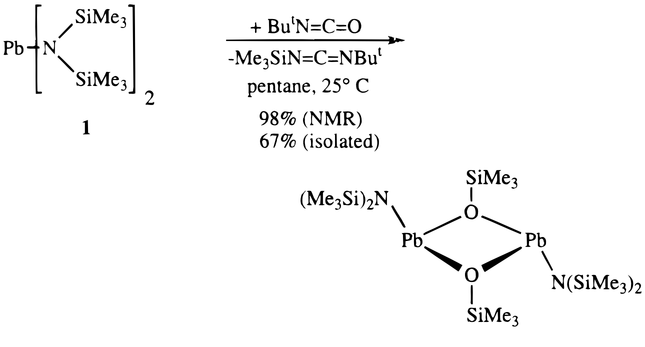


Figure 1. ORTEP drawing (30% thermal ellipsoids) of the molecular structure of **2**. Hydrogen atoms have been removed for clarity.

Scheme 1



2

dered rotation about the Pb−N bond was reached. After this point, two distinct resonances for different $-SiMe_3$ groups, one positioned over the four-membered ring and one directed away from it, began to emerge as the temperature approached, but did not reach due to technical limits, the slow exchange limit. This low Pb−N rotational barrier can be compared to that for the Sn−N bond in **5**, where the slow exchange limit occurs at room temperature.[11] Interestingly, as determined by NMR spectroscopy at 25 °C, compound **2** was found to be stable in solution for at least several weeks, during which time it did not disproportionate to **1** and **3**. This pronounced stability of **2** can be contrasted to that reported for the only other known inorganic heteroleptic lead(II) compound, $\{Pb[N(SiMe_3)_2][\mu\text{-}SC(SiMe_3)_3]\}_2$ (**6**), which has been shown to undergo irreversible dissociation in solution at 20 °C to **1** and $Pb[SC(SiMe_3)_3]_2$.[12]

Crystallographic analysis of **2** provided further proof for the proposed dimeric structure of this compound (see Figure 1).[13] In this regard, while the molecular structure of **2** possesses gross structural features that are similar to those found for **6** and other dimeric tin(II) metal complexes containing the $-N(SiMe_3)_2$ group, notable differences do exist.[11,12,16] Most importantly, the structure of **6** as reported by Lappert and co-workers[12] is highly asymmetric with quite different Pb−N bonds, whereas **2** is symmetric with a Pb−N bond length that is close to the mean value found for the former compound (*cf.* 2.07(5) and 2.35(5) Å for **6** vs 2.205(5) Å for **2**). This asymmetry in the structure of the Lappert compound **6** is further reflected in the quite different N−Si bond lengths found within a single $-N(SiMe_3)_2$ group where the longer of the two, 1.89 (6) Å, is unusually long and the other appears impossibly short at 1.55(5) Å (*cf.*, N−Si bond lengths of 1.63−1.74 Å in silylamines and metal silylamides[17]). Unfortunately, no comment was made by the authors regarding these structural irregularities. In **2**, a similar discrepancy in N−Si bond lengths is observed, however, now the difference between the two is much smaller, 1.711(12) *vs* 1.666(11) Å, and it is possible that the rotational disorder observed for C(1), C(2), and C(3) is responsible, at least partially, for this disparity.[13] In keeping with other structures bearing the $-N(SiMe_3)_2$ group, the geometries of the nitrogen atoms in **2** are best described as being trigonal planar (sum of bond angles around N, $\Sigma\theta_N = 359.9°$). Further, the four-membered ring of **2** is planar with O−Pb−O bond angles of 75.1(4)° and Pb−O−Pb bond angles of 104.9°. Here, the Pb atoms are pyramidally configured ($\Sigma\theta_{Pb} = 282.5°$), whereas the oxygen atoms are once again trigonal planar ($\Sigma\theta_O = 359.9°$). Finally, the nonbonded distance between the two Pb atoms in **2** is 3.6212(10) Å.

In contrast to our prior successes with using carbon dioxide metathesis for the high-yield synthesis of $[M(OSiMe_3)_2]_2$ for M = Ge and Sn,[8a] the reaction of **1** in pentane with CO_2 (60 psi) could not be controlled to provide the desired compound, $[Pb(OSiMe_3)_2]_n$ (**3**). Rather, it was found that although **1** reacted instantaneously with CO_2 at 25 °C, a white, pentane-insoluble material was initially produced that when isolated and characterized did not conform to **3**. Instead, this material routinely exhibited a singlet resonance in the ^1H NMR (benzene-d_6) spectrum that was found to shift, from reaction to reaction, within the limits of 0.22−0.25 ppm. Along with this variation, ^{207}Pb NMR spectra revealed resonances that also ranged from 800 ppm (broad) to 1188 ppm (sharp). Finally, apart from ruling out the presence of nitrogen, chemical analyses were quite inconsistent and did not point to any one pure compound being present. On the basis of these data, it was concluded that, although presumably formed, **3** undergoes rapid condensation under the reaction conditions to produce a mixture of higher nuclearity products of varying composition that are in rapid equilibration with one another. While this stands in sharp contrast to the reported robustness of **3** (mp 160 °C), obtained through an alternative procedure,[6c] it is important to note that Schmidbauer and Bergfeld[6b] have previously reported the likely existence of different interconverting

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(12) Hitchcock, P. B.; Jasim, H. A.; Kelly, R. E.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1776−1778.

(13) Single crystals of **2** are, at 218 K, monoclinic, $P2_1/c$, with a = 8.5329(2) Å, b = 19.24430(10) Å, c = 11.4783(3) Å, β = 110.198(10)°, V = 1768.94(6) Å^3, Z = 2, μ(Mo Kα) = 97.24 cm^{-1}, D_{calc} = 1.715 g/cm^3, and $R(F)$ = 6.97%, for 2090 observed independent reflections ($4° \le 2\theta \le 56°$). Empirical absorption corrections were applied using the program DIFABS.[14] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions.[15]

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oligomeric forms of **3** in solution, along with the observation that this compound begins to turn yellow at 110 °C and at 220 °C decomposes with formation of hexamethyldisiloxane. Unfortunately, using 2 equiv of Bu^tNCO in place of CO_2 for the metathesis of **1** provided a similar white pentane-insoluble material, as did the reaction of **2** with 2 equiv of Bu^tNCO. These data are consistent with the view that compound **3** is very susceptible to impurity- and, most especially, base-induced condensations, and in fact, it may be that the nucleophilicities of both CO_2 and Bu^tNCO are sufficient to promote these transformations. Alternatively, it is possible that the heterocumulene metathesis process produces either a monomer or an open dimer (trimer) of **3**, which is then even more highly prone toward undergoing condensation. This latter idea is suggested by previous results regarding the heterocumulene metathesis of the tin(II) dimer **5** with Bu^tNCO that was shown to proceed via formation of the open dimer $[(Bu^tNCO)(Me_3SiO)Sn](\mu\text{-}OBu^t)[Sn(OBu^t)(OSiMe_3)]$.[8b]

Although **3** could not be obtained by metathesis, it was interestingly found that if the initially formed insoluble material was not immediately isolated, within a short period of time after its formation (~10−15 min), it would disappear to leave a final clear pentane solution. Removal of the solvents in vacuo then left a white crude product that appeared to now consist primarily of a single compound by ^1H and ^{207}Pb NMR spectroscopy. It was also later found that this compound could be obtained in pure form by simply carrying out the metathesis of **1** in toluene, followed by heating the reaction mixture to 80 °C for 1 h. Recrystallization from toluene at −40 °C then provided an analytically pure material for which spectroscopic, chemical, and crystallographic analyses provided data that were fully consistent with it being the heptanuclear lead(II) oxo cluster $Pb_7(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu\text{-}OSiMe_3)_{10}$ (**4**).[18,19] Thus, a ^{207}Pb NMR spectrum of **4** taken at 25 °C showed that this compound contains three magnetically inequivalent lead environments, as indicated by sharp resonances occurring at 339.6, 628.4, and 1129.8 ppm (relative to $PbEt_4$) in an approximate 3:3:1 ratio, with each one possessing distinct coupling satellites ($^2J(^{207}Pb-^{207}Pb)$ = 367 Hz). A ^1H NMR spectrum also revealed several different environments for the $-OSiMe_3$ groups of **4**, though these appear to be involved, to some extent, in rapid exchange between sites at 25 °C. Interestingly, heating a toluene solution of **4** to 100 °C for 18 h left this compound unchanged and this observed stability is in keeping with variable-temperature NMR studies, which suggest that the Pb−O-bonded framework of **4** does not dissociate at this temperature. In this regard, it is important to note that the thermal stability of **4** stands in stark contrast to the case for other lead(II) oxo clusters, such as $Pb_4(\mu_4\text{-}O)(\mu\text{-}OPr^i)_6$ and $Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OBu^t)_4$, which are known to engage in dissociative equilibria.[1d,f]

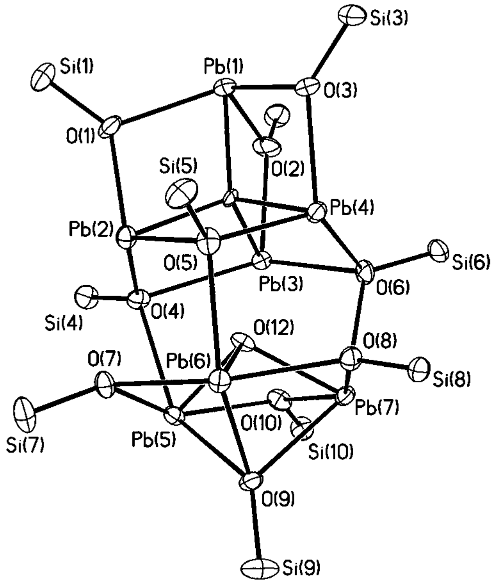

Figure 2. ORTEP drawing (30% thermal ellipsoids) of the molecular structure of **4**. Methyl groups have been omitted for clarity.

As Figure 2 reveals, the molecular structure of **4** closely approximates C_{3v} symmetry and it indeed possesses three different sets of Pb atoms that correspond to those observed in its ^{207}Pb NMR spectrum. Curiously, one set (Pb(5)−Pb(7)) consists of Pb atoms in an unusual five-coordinate environment, whereas the other two sets (Pb(1) and Pb(2)−Pb(4)) have the more commonly encountered tetracoordinate configurations.[20] The structure also possesses two differently coordinated oxo groups, μ_3-O and a μ_4-O, which can be viewed as residing in the interior of a Pb−O-bonded cage.[20] The Pb−O bond lengths fall into different categories depending upon the environment of the oxygen atom. For instance, these values are the shortest for bonds made to the μ_3-O and μ_4-O atoms (*cf.* mean Pb−O of 2.263(8) and 2.270(8) Å, respectively), whereas the longest are surprisingly found for the six-membered ring composed of O(4), O(5), O(6), Pb(2), Pb(3), and Pb(4), which has an alternating short−long Pb−O pattern (*cf.*, mean of long Pb−O, 2.660(9) Å; mean of short Pb−O, 2.401(9) Å). Finally, the nonbonded distances between lead atoms in the fragment containing Pb(1)−Pb(4) are significantly longer than those in the fragment containing Pb(5)−Pb(7) (*cf.* mean of 3.679(7) vs 3.443(7) Å).[21]

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[18] Data for **4**: ^1H NMR (25° C, benzene-d_6) δ 0.21−0.25 (br m, 72H), 0.36 (br s, 18H); $^{207}Pb\{^1H\}$ NMR (25 °C, benzene-d_6) δ 339.6, 628.4, 1129.8, $^{13}C\{^1H\}$ NMR (25 °C, benzene-d_6) δ 2.31, 3.61, 4.19. Anal. Calcd for $C_{30}H_{90}O_{12}Pb_7Si_{10}\cdot(toluene)_{0.5}$:[18] C, 16.62; H, 3.91. Found: C, 16.53; H, 3.85.

[19] Single crystals of $\mathbf{4}\cdot C_7H_8$ (toluene) are, at 223 K, monoclinic, $P2_1/n$, with $a = 17.1222(4)$ Å, $b = 20.3681(4)$ Å, $c = 21.5244(5)$ Å, $\beta = 90.9260(10)°$, $V = 7505.6(3)$ Å^3, $Z = 4$, $\mu(\text{Mo K}\alpha) = 158.43$ cm^{-1}, $D_{calc} = 2.183$ g/cm^3, and $R(F) = 5.41\%$, for 9365 observed independent reflections ($4° \leq 2\theta \leq 56°$). Empirical absorption corrections in both cases were applied using the program DIFABS.[14] Non-hydrogen atoms were refined anisotropically, except for the carbon atoms in the solvent molecule of toluene. Hydrogen atoms were treated as idealized contributions.[15]

[20] The mean of the nonbonded distances between the pairs of atoms, Pb(2)···O(7), Pb(3)···O(10), and Pb(4)···O(8) is 2.90 Å. The mean of the nonbonded distances between the pairs of atoms Pb(2)···O(12), Pb(3)···O(12), and Pb(4)···O(12), is 2.96 Å.

[21] This work was supported in part by the MRSEC program under the National Science Foundation (Grant No. DMR-9400379).