Synthesis and structural characterization of tricarbomethoxymethanate complexes of copper(II) and barium(II) and evaluation of their suitability for MOCVD applications†

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The reaction between $Cu(OCH_3)_2$ and HL [$L = {}^{-}C(CO_2CH_3)_3$] in THF gives a mixture of two products, $CuL(OCH_3)$ and $CuL_2(THF)_2$. $CuL(OCH_3)$ was characterized by elemental analysis, infrared spectroscopy and thermal decomposition studies, and its insolubility in THF, at room temperature, suggests that it may be polymeric. The solid state structure of $CuL_2(THF)_2$ was established *via* a single-crystal X-ray diffraction analysis. This complex has a tetragonally distorted *trans*-disubstituted octahedral structure with L binding like a conventional *bidentate* β-diketonate ligand; the central CO_2CH_3 group of each L is not coordinated. $CuL_2(THF)_2$ readily loses the two THF molecules bound to the Cu(II) center upon drying in a stream of dinitrogen to produce THF-free CuL_2. Alternatively, THF-free CuL_2 can be prepared by the reaction of $CuL(OCH_3)$ with HL in refluxing toluene. X-ray crystallography shows that CuL_2 is a polymeric solid composed of a planar $Cu(\eta^2\text{-}L)_2$ repeat unit in which the central CO_2CH_3 group of each L binds weakly to the Cu(II) center of a neighboring unit along a "stepped" (displaced) stack of CuO_4 units. The reaction between elemental barium and HL in THF requires activation with $NH_{3(g)}$. The product is a white solid of empirical formula $BaL_2 \cdot 0.36THF$. It was characterized by elemental analysis, ^{1}H NMR, $^{13}C\{^1H\}$ NMR, and infrared spectroscopies, and thermal decomposition studies. It is insoluble in common laboratory solvents but soluble in strong Lewis bases such as pyridine, dimethylsulfoxide, and hexamethylphosphoramide (HMPA). The product resulting from the depolymerization of $BaL_2 \cdot 0.36THF$ with HMPA was characterized *via* a single-crystal X-ray diffraction analysis. It is a dimer of empirical formula $Ba_2L_4(HMPA)_4$. It consists of two $BaL_2(HMPA)_2$ fragments linked together, in a centrosymmetric fashion, by two μ^2,η^3-[${}^{-}C(CO_2CH_3)_3$] ligands; this is made possible by the utilization of the donor power of the pendant $C(O)OCH_3$ group not used in $CuL_2(THF)_2$. The remaining two ${}^{-}C(CO_2CH_3)_3$ ligands are also bidentate but are non-bridging, and the four HMPA molecules are bonded through oxygen, resulting in a coordination number of seven for each barium. CuL_2 is volatile and sublimes upon heating the amorphous material obtained from spontaneous desolvation of $CuL_2(THF)_2$, or polymeric CuL_2, or $CuL(OCH_3)$ under high vacuum. The barium complexes are not volatile. Metallic copper is obtained upon heating the Cu(II) complexes to 1000 °C in a stream of argon, and formation of CuO results when these complexes are decomposed in the presence of oxygen. Thermal decomposition of $BaL_2 \cdot 0.36THF$ and $Ba_2L_4(HMPA)_4$ has been carried out under argon and O_2–Ar atmospheres; residues containing varying amounts of BaO, BaO_2 and $BaCO_3$ were obtained depending on the experimental conditions.

Since the publication of the book *Metal β-Diketonates and Allied Derivatives* in 1978,[1] numerous reports have appeared in the literature concerning the synthesis, characterization, and use of such complexes for the preparation of thin films of metals and oxide-based materials *via* MOCVD (metal-organic chemical vapor deposition). This is because acetylacetone and its analogues are known to produce metal complexes that are chemically and thermally robust and, in some cases, quite volatile.[2–5]

The preference of divalent metals for coordination numbers higher than four has led to a strategy of covalently binding a neutral donor (*e.g.* ether or amine) "tail" to the β-diketonate or β-ketoiminate ligand.[6] We continue this theme here by using a β-diketonate ligand whose central backbone position bears an ester substituent. Tricarbomethoxymethane, $HC(CO_2CH_3)_3$ (**1**), is an analogue of acetylacetone that is readily prepared from the reaction between $NaCH(CO_2CH_3)_2$ and $ClCO_2CH_3$.[7] Despite the ease of access to this ligand, only one report was found in the literature that describes the utilization of the deprotonated form of tricarbomethoxymethane, namely in the preparation of transition metal phosphine complexes of Ni(II).[8] In this report, no mention was made of the coordination chemistry of the tricarbomethoxymethanate anion, ${}^{-}C(CO_2CH_3)_3$. Tricarbomethoxymethane possesses some features additional to those of acetylacetone and related molecules that make it a ligand worthy of investigation. First, one might wonder if the presence of methoxy substituents on a β-diketonate ligand has any effect on the complexing ability of this moiety. Second, the possibility exists that the presence of the third carbonyl group might lead to complexes with unusual shapes in which the

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† Electronic supplementary information (ESI) available: complete crystallographic and experimental details, positional and anisotropic thermal parameters, and full tables of bond lengths and angles for compounds **3**, **4′** and **6**. See http://www.rsc.org/suppdata/nj/b0/b008147g/

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tricarbomethoxymethanate anion binds to a metal center in a threefold symmetric fashion *via* three identical oxygens or even through the central carbon atom. Lastly, it is of interest to determine if the thermal decomposition of tricarbomethoxymethanate complexes differs from that of acetylacetonate complexes, especially in terms of the mechanism of formation (*i.e.* production of intermediate phases) and nature of the resulting ceramic material. Indeed, changes in the nature of the ceramic product as a result of ligand manipulation have been observed in the case of carboxylate complexes of barium.[3]

We report herein the synthesis and characterization of monomeric, dimeric, and polymeric tricarbomethoxymethanate complexes of copper(II) and barium(II). Furthermore, these complexes have been subjected to thermolysis and volatility studies to assess their suitability as precursors for MOCVD applications.

Results and discussion

Synthesis, characterization and physical properties of copper(II) complexes

The reaction between 2 equiv. of **1** and polymeric $\mathrm{Cu(OCH_3)_2}$, at room temperature, in THF, yields two products. The first product, compound **2**, is a pale blue precipitate that is insoluble in THF at room temperature. The exact structure of **2** is unclear, but its insolubility in THF suggests that it may be polymeric. Results from elemental analysis for C, H, N and Cu and thermal decomposition studies under argon suggest that the chemical formula of **2** is $\mathrm{Cu[C(CO_2CH_3)_3][OCH_3]}$. The second reaction product, compound **3**, is soluble in THF. It crystallizes as green crystals upon layering of the reaction mixture with hexanes. Its empirical formula is $\mathrm{Cu[C(CO_2CH_3)_3]_2[THF]_2}$ based on results from a single-crystal X-ray diffraction study. Interestingly, we have found that **3** readily loses the two THF molecules upon drying *in vacuo* or in a stream of dinitrogen. The resulting green amorphous solid, compound **4**, may be formulated as $\mathrm{Cu[C(CO_2CH_3)_3]_2}$ based on results from elemental analysis for C, H, N and Cu and thermal decomposition studies under argon.

Additional experiments aimed at better characterizing complex **2** have been carried out: **2** is converted to an emerald green solid upon refluxing with 1 equiv. of **1** in toluene and removing the methanol produced in the reaction *via* azeotropic distillation. The emerald green solid was characterized as polymeric $\mathrm{Cu[C(CO_2CH_3)_3]_2}$ (**4′**) by X-ray crystallography. Interestingly, neither **3** nor **4′** are obtained when compound **2** is refluxed in toluene or THF in the absence of tricarbomethoxymethane. Instead, complex **2** is quantitatively recovered upon cooling of the clear toluene and THF solutions. These results suggest that, in the above reaction, **4′** is formed according to eqn. (1) rather than eqn. (2):

$$\underset{\mathbf{2}}{\mathrm{Cu[C(CO_2CH_3)_3][OCH_3]}} + \underset{\mathbf{1}}{\mathrm{HC(CO_2CH_3)_3}} \rightarrow \underset{\mathbf{4'}}{\mathrm{Cu[C(CO_2CH_3)_3]_2}} + \mathrm{CH_3OH} \quad (1)$$

$$2\,\underset{\mathbf{2}}{\mathrm{Cu[C(CO_2CH_3)_3][OCH_3]}} \rightarrow \underset{\mathbf{4'}}{\mathrm{Cu[C(CO_2CH_3)_3]_2}} + \mathrm{Cu(OCH_3)_2} \quad (2)$$

X-Ray crystallographic study of $\mathrm{Cu[C(CO_2CH_3)_3]_2[THF]_2}$ (3). X-Ray crystallography shows $\mathrm{Cu[C(CO_2CH_3)_3]_2[THF]_2}$ to be monomeric in the solid state. It is a distorted octahedral molecule with a rigorous center of inversion, but an inner coordination sphere of idealized D_{2h} symmetry (Fig. 1). The Cu–O(chelate) distances, 1.9423(15) and 1.9569(15) Å, are nearly 0.5 Å shorter than the very long bonds to THF [2.4048(16) Å]. Such long bonds (Table 1) are consistent with the THF oxygens being pyramidal (the sum of the bond angles around oxygen is 343.7°). In view of these long bonds, it is not surprising to find that this complex readily loses the two THF molecules upon drying. The conformations of the THF rings are staggered with respect to the chelate oxygens. The uncoordinated ester group [that involving C(11)] is perpendicular to the chelate ring plane, and the methoxy groups involving O(7) and O(9) bend away from the carbomethoxy group containing C(11); these conformations minimize mutual repulsions. The methyl groups C(8) and C(10) are *syn* to O(2) and O(6), and thus prevent these oxygens from bridging to a second metal. As shown in Scheme 1, the ring C–C bonds are shortened (consistent with conjugation) and the longer C(4)–C(11) distance suggests that this carbomethoxy group is not conjugated with the other two. Consistent with this conclusion, the bond length of the pendant C=O group, C(11)–O(12), is considerably shorter than the distances C(3)–O(2) and C(5)–O(6). All three methoxy groups have identical C–OCH$_3$ bond lengths, and these are consistent with single bonds.

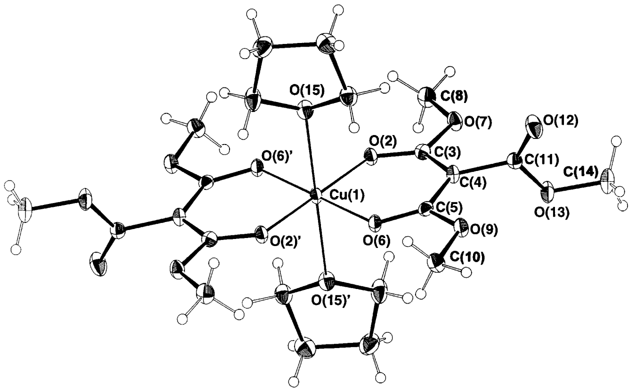


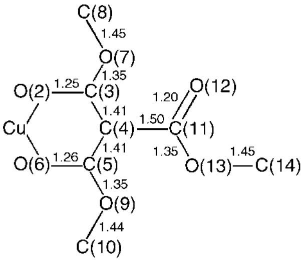
Fig. 1 Molecular structure of $\mathrm{Cu[C(CO_2CH_3)_3]_2[THF]_2}$ (**3**) showing 50% probability ellipsoids and the atom numbering scheme used in the tables.

X-Ray crystallographic study of $\mathrm{Cu[C(CO_2CH_3)_3]_2}$ (4′). X-Ray crystallography shows that $\mathrm{Cu[C(CO_2CH_3)_3]_2}$ is polymeric in the solid state. In this polymer, the coordinated THF

Table 1 Selected bond lengths (Å) and angles (°) for $\mathrm{Cu[C(CO_2Me)_3]_2[THF]_2}$ (**3**)[a]

Cu(1)–O(2)	1.9423(15)	O(12)–C(11)	1.1976(28)
Cu(1)–O(6)	1.9569(15)	O(13)–C(11)	1.3463(28)
Cu(1)–O(15)	2.4048(16)	O(13)–C(14)	1.452(3)
O(2)–C(3)	1.2529(27)	O(15)–C(16)	1.438(3)
O(6)–C(5)	1.2570(27)	O(15)–C(19)	1.432(3)
O(7)–C(3)	1.3455(26)	C(3)–C(4)	1.411(3)
O(7)–C(8)	1.4490(28)	C(4)–C(5)	1.407(3)
O(9)–C(5)	1.3511(27)	C(4)–C(11)	1.495(3)
O(9)–C(10)	1.4414(28)		
O(2)–Cu(1)–O(6)	92.06(6)	O(2)–C(3)–O(7)	118.81(20)
O(2)–Cu(1)–O(6)′	87.94(6)	O(2)–C(3)–C(4)	127.77(20)
O(2)–Cu(1)–O(15)	90.01(6)	O(7)–C(3)–C(4)	113.41(19)
O(2)–Cu(1)–O(15)′	89.99(6)	C(3)–C(4)–C(5)	120.81(20)
O(6)–Cu(1)–O(15)	91.60(6)	C(3)–C(4)–C(11)	118.80(19)
O(6)–Cu(1)–O(15)′	88.40(6)	C(5)–C(4)–C(11)	120.38(20)
Cu(1)–O(2)–C(3)	125.65(15)	O(6)–C(5)–O(9)	118.50(19)
Cu(1)–O(6)–C(5)	125.38(14)	O(6)–C(5)–C(4)	127.68(21)
C(3)–O(7)–C(8)	116.68(18)	O(9)–C(5)–C(4)	113.81(19)
C(5)–O(9)–C(10)	116.96(18)	O(12)–C(11)–O(13)	122.91(21)
C(11)–O(13)–C(14)	114.93(19)	O(12)–C(11)–C(4)	125.45(21)
Cu(1)–O(15)–C(16)	118.37(14)	O(13)–C(11)–C(4)	111.64(19)
Cu(1)–O(15)–C(19)	119.38(14)	O(15)–C(16)–C(17)	105.21(20)
C(16)–O(15)–C(19)	105.97(18)	O(15)–C(19)–C(18)	105.92(21)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.



Scheme 1

molecules present in $Cu[C(CO_2CH_3)_3]_2[THF]_2$ have been replaced by carbonyl oxygens of ester groups from neighboring molecules. The resulting polymeric chains have the step-ladder structure shown in Fig. 2(a) in which the axial Cu–O distances, 2.583 Å, are the shortest contacts between neighboring molecules. At the molecular level (Fig. 3), the Cu–O(chelate) distances found in polymeric $Cu[C(CO_2CH_3)_3]_2$ are approximately 0.03 Å shorter (Table 2) than those in complex **3**, and this tallies with the decrease in strength of the Cu–O interactions in the axial positions. There are, however, no significant differences in the C=O and C–C bond lengths of the chelate rings between the two complexes. Interaction of the third carbomethoxy group with the Cu(II) center from a neighboring molecule is made possible by a degree of conjugation of this group with the chelating carbomethoxy moieties, which allows for partial delocalization of the negative charge onto this group. The following observations are consistent with this: the C(4)–C(11) bond length in complex **4′**, 1.48 Å, is about 0.02 Å shorter than that found in complex **3**. The C(11)–O(12) distance in $Cu[C(CO_2CH_3)_3]_2$, 1.22 Å, is approximately 0.02 Å longer than that found in $Cu[C(CO_2CH_3)_3]_2[THF]_2$. Also, the plane formed by C(11), O(12) and O(13) is no longer perpendicular to the chelate ring plane [Fig. 2(b)], as it is in $Cu[C(CO_2CH_3)_3]_2[THF]_2$. This is necessary to "reach" the neighboring copper atom in the stepped stack.

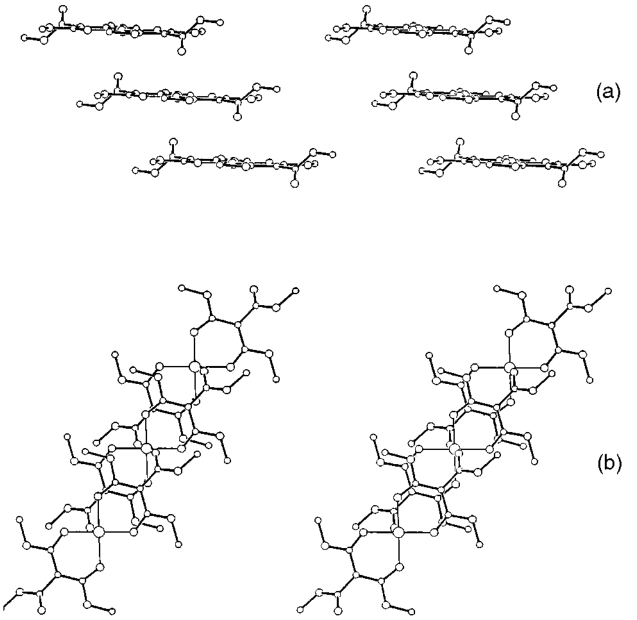


Fig. 2 Stereoview of the polymeric chain of $Cu[C(CO_2CH_3)_3]_2$ (**4′**) with the hydrogen atoms omitted for clarity: (a) viewed from the side, (b) viewed from the top.

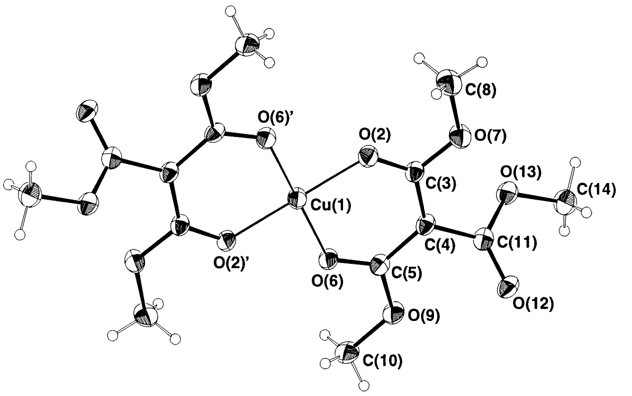


Fig. 3 ORTEP drawing of the repeat unit of $Cu[C(CO_2CH_3)_3]_2$ (**4′**) showing 50% probability ellipsoids and the atom numbering scheme used in the tables.

Table 2 Selected bond lengths (Å) and angles (°) for $Cu[C(CO_2Me)_3]_2$ (**4′**)[a]

Cu(1)–O(2)	1.9111(13)	O(9)–C(10)	1.4447(25)
Cu(1)–O(6)	1.9244(12)	O(12)–C(11)	1.2160(22)
O(2)–C(3)	1.2489(21)	O(13)–C(11)	1.3467(23)
O(6)–C(5)	1.2529(21)	O(13)–C(14)	1.4382(24)
O(7)–C(3)	1.3422(22)	C(3)–C(4)	1.4224(23)
O(7)–C(8)	1.4575(22)	C(4)–C(5)	1.4169(25)
O(9)–C(5)	1.3441(20)	C(4)–C(11)	1.4768(24)
O(2)–Cu(1)–O(6)	91.56(5)	C(3)–C(4)–C(5)	119.20(15)
O(2)–Cu(1)–O(6)′	88.44(5)	C(3)–C(4)–C(11)	122.03(16)
Cu(1)–O(2)–C(3)	127.49(12)	C(5)–C(4)–C(11)	118.77(15)
Cu(1)–O(6)–C(5)	126.72(12)	O(6)–C(5)–O(9)	117.43(16)
C(3)–O(7)–C(8)	115.43(15)	O(6)–C(5)–C(4)	127.33(16)
C(5)–O(9)–C(10)	116.28(15)	O(9)–C(5)–C(4)	115.17(15)
C(11)–O(13)–C(14)	115.57(16)	O(12)–C(11)–O(13)	121.75(17)
O(2)–C(3)–O(7)	117.28(15)	O(12)–C(11)–C(4)	126.26(18)
O(2)–C(3)–C(4)	127.18(17)	O(13)–C(11)–C(4)	111.97(15)
O(7)–C(3)–C(4)	115.53(15)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Synthesis, characterization and physical properties of barium(II) complexes

Although the acidity of the methine hydrogen of tricarbomethoxymethane (**1**) is quite high, there is no visible reaction, at room temperature and in THF, between 2 equiv. of **1** and barium granules. The reason for the lack of reaction is well-documented and comes from the inertness of elemental barium when used in the form of granules.[9–13] No perceptible reaction occurs upon refluxing 2 equiv. of **1** with elemental barium in benzene for 18 h. A similar reaction performed in refluxing THF for 66 h gives the desired barium complex in 21% yield. No noticeable improvements are brought about when sonication is used instead of refluxing in the above reactions. However, a moderate H_2 evolution is observed after ammonia is bubbled for 15 min into a THF solution containing **1** and suspended barium granules. The way in which $NH_{3(g)}$ promotes reaction between barium granules and ligands bearing acidic hydrogens is not fully understood, but the formation of transient species such as barium amide[9–12] or solvated electrons[13] has been suggested. Concomitant with H_2 evolution, a white precipitate forms. We have observed similar precipitates with other very acidic ligands such as $HC_5(CO_2CH_3)_5$ and $HC(COCH_3)_3$, but not with less acidic ligands such as silanols,[9,12] alcohols[11,12] and $HN(SiMe_3)_2$.[10] The white precipitate is believed to be the ammonium salt of **1** and may be at the origin of the small amount of nitrogen present in the final product (see Experimental). Furthermore, the insolubility of the ammonium salt of **1** in THF may be one of the factors responsible for the extended reaction time. We havealso observed that the reaction between **1** and barium granules slows down and, eventually, stops when, after activation with $NH_{3(g)}$, the mixture is stirred under an inert atmosphere of dinitrogen. This does not happen when a slow purge of $NH_{3(g)}$ is maintained above the mixture during the reaction period.

The product of the reaction, compound **5**, is a fine white powder of empirical formula $Ba[C(CO_2CH_3)_3]_2 \cdot 0.36THF$. The presence of THF in the compound is clearly evidenced in both ^1H and $^{13}C\{^1H\}$ NMR experiments and agrees well with the results from the elemental analysis. The amount of THF may vary slightly from one batch to the next but is always around 0.3 molecule of THF per $Ba[C(CO_2CH_3)_3]_2$ unit. Compound **5** is insoluble in nonpolar solvents and shows no appreciable solubility in refluxing THF and refluxing dimethoxyethane. However, it dissolves readily in the presence of strong Lewis bases such as pyridine, DMSO (dimethylsulfoxide) and HMPA (hexamethylphosphoramide). These observations, combined with the fact that **5** shows no volatility, strongly suggest a polymeric structure in the solid state.

We sought to obtain a soluble form of **5**. HMPA has been shown to be very effective at solubilizing barium-containing aggregates.[11] Consequently, compound **5** was suspended in a 1 : 10 v/v solution of HMPA and toluene, and the mixture was refluxed for 1 h. A clear solution was obtained which, upon removal of the toluene, addition of *n*-pentane and cooling to −15 °C, yielded colorless needles. The needles, compound **6**, were characterized as $Ba_2[C(CO_2CH_3)_3]_4[HMPA]_4$ by single-crystal X-ray diffraction, elemental analysis, and NMR and infrared spectroscopies.

The thermodynamic stability of dimer **6** is certainly quite high as it was prepared under conditions, namely reflux and excess of HMPA, that were expected to lead to monomer formation. In spite of this apparent stability, however, the HMPA molecules do not seem to be tightly bound to the barium centers in the solid state. Indeed, it is found that when compound **6** is dried *in vacuo* for long periods of time, elemental analysis of the resulting powder shows a deficiency of HMPA. Also, we have found that it is possible to extract the HMPA from dimer **6** by simply stirring the solid in benzene. Thirdly, the material visibly undergoes a solid state transformation, ascribed to HMPA dissociation, between 71 and 78 °C. Analysis of compound **6** by differential scanning calorimetry (DSC) supports this interpretation in that an irreversible process with a negative heat flow is observed in a narrow temperature range around 80 °C. This endotherm is not observed in the DSC curve of compound **5**. Sublimation experiments under high vacuum indicate that **6** is not volatile.

Solid state structure of $Ba_2[C(CO_2CH_3)_3]_4[HMPA]_4$ (6). This structure is considerably more complex than those of the copper(II) compounds discussed above, as a result of the higher coordination number adopted by the larger Ba^{2+} ion.[14] This higher coordination number is in part satisfied by the utilization of the donor power of the carbomethoxy group that remains unused in $Cu[C(CO_2CH_3)_3]_2[THF]_2$ (**3**). There are two molecules in the unit cell and two independent half-molecules in the asymmetric unit of the barium complex; the shortest contact between the two molecules is 3.012 Å and the intramolecular Ba···Ba distances are 6.881 and 6.975 Å. In each half-molecule, the barium center achieves a coordination number of six *via* interaction with two η^2-$[^-C(CO_2CH_3)_3]$ anions and two HMPA molecules, similarly to the situation in compound **3**. Unlike **3**, however, one pendant $C(O)OCH_3$ group bridges, *via* the carbonyl oxygen, to barium in an adjacent molecule. This occurs in a complementary fashion to produce a centrosymmetric dimer (not a polymer) in which the barium centers are seven-coordinate (Fig. 4). In this dimer, the HMPA molecules presumably occupy positions that were occupied by bridging carbomethoxy groups in the original polymer (**5**).

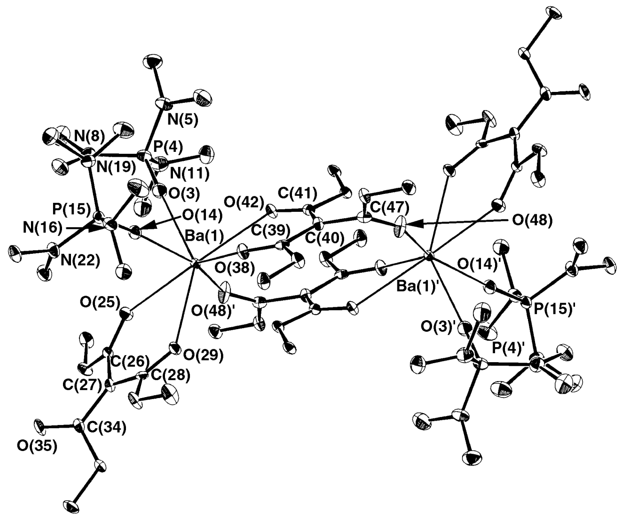


Fig. 4 ORTEP drawing of one molecule of $Ba_2[C(CO_2CH_3)_3]_4[HMPA]_4$ (**6**) showing 30% probability ellipsoids and the atom numbering scheme used in the tables.

In contrast to **3**, the distances between the metal and the neutral donor (HMPA) molecules are the shortest metal–ligand distances in the complex (Table 3). The Ba–O(chelate) bond lengths vary from 2.684(4) to 2.770(4) Å, and the Ba–O(pendant carboxymethyl) distances are 2.715(4) and 2.766(4) Å; the barium–oxygen bond lengths are thus variable, in addition to being long. This disparity in the Ba–O bond lengths is less pronounced than that observed for thd complexes of barium (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) in which barium is seven-coordinate.[15] In $[Ba(thd)_2 \cdot Et_2O]_2$,[15b] the Ba–O distances span the range 2.567(5) to 2.827(6) Å. This latter distance corresponds to the Ba–OEt_2 distance. In $Ba(thd)_2(CH_3OH)_3 \cdot CH_3OH$,[15c] the Ba–O(neutral donor) distances are once again the longest Ba–O distances in the complex; they are in the range 2.775(8)–2.822(5) Å. The Ba–O(thd) bond lengths are in the range 2.578(5)–2.739(5) Å. Also, two additional weak Ba–O interactions of 3.321(5) and 3.699(7) Å are present. Only one crystallographically unique barium atom is thought to be seven-coordinate in the room temperature structure of $Ba_4(thd)_8$; the second unique barium atom is six-coordinate.[15d,e] The Ba–O distances as reported by Gleizes *et al.*[15d] for the seven-coordinate barium atom are in the range 2.531(21)–2.950(21) Å and those published by Drozdov and Trojanov[15e] range from 2.58(2) to 2.927(8) Å. In the low temperature (150 K) structure of $Ba_4(thd)_8$,[15f] the two crystallographically unique barium atoms are proposed to be seven-coordinate; the Ba–O distances are in the range 2.584(6)–2.906(6) Å for the first barium atom and in the range 2.479(5)–3.140(6) Å for the second.

Ba–O(HMPA)–P(HMPA) bond angles are quite variable [154.2(2)–175.8(2)°], but the Ba–O bond lengths [2.618(4)–2.642(4) Å] are not; this indicates that HMPA–Ba bonds are not strongly directional.

There are no statistically significant differences in bond lengths between η^2 and η^3,μ chelates in this molecule. There is likewise no significant difference in C=O distances among the chelates, nor among the C(trigonal)–$C(O)OCH_3$ distances. All of these observations are consistent with the conclusion that Ba^{2+} perturbs the chelate ligand less than does Cu^{2+}.

Volatility data

The amorphous material **4** obtained from spontaneous desolvation of $Cu[C(CO_2CH_3)_3]_2[THF]_2$ (**3**) sublimes without decomposition in the range 138–173 °C under 5×10^{-5} Torr. Polymeric $Cu[C(CO_2CH_3)_3]_2$ (**4′**) sublimes with partial decomposition to Cu^0 in the range 140–176 °C under 6×10^{-5} Torr. $Cu[C(CO_2CH_3)_3][OCH_3]$ (**2**) slowly decom-

Table 3 Selected bond lengths (Å) and angles (°) for $Ba_2[C(CO_2Me)_3]_4[HMPA]_4$ (**6**)[a]

Ba(1)–O(3)	2.630(4)	O(48)–C(47)	1.205(6)
Ba(1)–O(14)	2.642(4)	O(49)–C(47)	1.352(6)
Ba(1)–O(25)	2.703(4)	O(49)–C(50)	1.430(7)
Ba(1)–O(29)	2.698(4)	O(73)–C(74)	1.235(6)
Ba(1)–O(38)	2.770(4)	O(77)–C(76)	1.215(6)
Ba(1)–O(42)	2.690(4)	O(78)–C(74)	1.369(6)
Ba(1)–O(48)′	2.766(4)	O(78)–C(79)	1.420(7)
Ba(2)–O(51)	2.630(4)	O(80)–C(76)	1.365(7)
Ba(2)–O(62)	2.618(4)	O(80)–C(81)	1.425(7)
Ba(2)–O(73)	2.737(4)	O(83)–C(82)	1.209(7)
Ba(2)–O(77)	2.684(4)	O(84)–C(82)	1.359(7)
Ba(2)–O(86)	2.762(4)	O(84)–C(85)	1.442(7)
Ba(2)–O(90)	2.760(4)	O(86)–C(87)	1.212(6)
Ba(2)–O(96)′	2.715(4)	O(90)–C(89)	1.231(6)
P(4)–O(3)	1.475(4)	O(91)–C(87)	1.380(6)
P(15)–O(14)	1.465(4)	O(91)–C(92)	1.440(6)
P(52)–O(51)	1.473(4)	O(93)–C(89)	1.350(6)
P(63)–O(62)	1.489(4)	O(93)–C(94)	1.436(7)
O(25)–C(26)	1.231(6)	O(96)–C(95)	1.219(6)
O(29)–C(28)	1.232(6)	O(97)–C(95)	1.354(7)
O(30)–C(26)	1.345(6)	O(97)–C(98)	1.451(7)
O(30)–C(31)	1.436(7)	C(26)–C(27)	1.451(8)
O(32)–C(28)	1.362(6)	C(27)–C(28)	1.410(8)
O(32)–C(33)	1.427(7)	C(27)–C(34)	1.460(8)
O(35)–C(34)	1.200(6)	C(39)–C(40)	1.444(8)
O(36)–C(34)	1.375(7)	C(40)–C(41)	1.421(8)
O(36)–C(37)	1.441(7)	C(40)–C(47)	1.465(8)
O(38)–C(39)	1.209(6)	C(74)–C(75)	1.434(8)
O(42)–C(41)	1.237(6)	C(75)–C(76)	1.430(8)
O(43)–C(39)	1.371(6)	C(75)–C(82)	1.459(8)
O(43)–C(44)	1.442(7)	C(87)–C(88)	1.436(8)
O(45)–C(41)	1.379(6)	C(88)–C(89)	1.448(7)
O(45)–C(46)	1.439(6)	C(88)–C(95)	1.456(8)
O(3)–Ba(1)–O(14)	77.93(13)	O(51)–Ba(2)–O(77)	83.36(12)
O(3)–Ba(1)–O(25)	85.65(12)	O(51)–Ba(2)–O(86)	81.18(12)
O(3)–Ba(1)–O(29)	143.19(12)	O(51)–Ba(2)–O(90)	120.79(12)
O(3)–Ba(1)–O(38)	120.74(13)	O(51)–Ba(2)–O(96)′	79.83(12)
O(3)–Ba(1)–O(42)	84.00(12)	O(62)–Ba(2)–O(73)	86.86(11)
O(3)–Ba(1)–O(48)′	85.65(13)	O(62)–Ba(2)–O(77)	83.11(12)
O(14)–Ba(1)–O(25)	86.91(12)	O(62)–Ba(2)–O(86)	111.57(12)
O(14)–Ba(1)–O(29)	83.70(12)	O(62)–Ba(2)–O(90)	76.72(11)
O(14)–Ba(1)–O(38)	74.30(12)	O(62)–Ba(2)–O(96)′	153.23(12)
O(14)–Ba(1)–O(42)	111.90(12)	O(73)–Ba(2)–O(77)	61.49(11)
O(14)–Ba(1)–O(48)′	154.97(12)	O(73)–Ba(2)–O(86)	134.56(11)
O(25)–Ba(1)–O(29)	61.56(11)	O(73)–Ba(2)–O(90)	88.68(11)
O(25)–Ba(1)–O(38)	142.09(11)	O(73)–Ba(2)–O(96)′	97.57(12)
O(25)–Ba(1)–O(42)	155.97(11)	O(77)–Ba(2)–O(86)	156.60(11)
O(25)–Ba(1)–O(48)′	72.99(12)	O(77)–Ba(2)–O(90)	144.86(11)
O(29)–Ba(1)–O(38)	83.51(11)	O(77)–Ba(2)–O(96)′	76.07(12)
O(29)–Ba(1)–O(42)	132.68(11)	O(86)–Ba(2)–O(90)	58.47(11)
O(29)–Ba(1)–O(48)′	99.00(13)	O(86)–Ba(2)–O(96)′	83.96(11)
O(38)–Ba(1)–O(42)	60.75(11)	O(90)–Ba(2)–O(96)′	129.56(11)
O(38)–Ba(1)–O(48)′	130.69(11)	Ba(1)–O(3)–P(4)	166.17(27)
O(42)–Ba(1)–O(48)′	84.63(12)	Ba(1)–O(14)–P(15)	175.79(24)
O(51)–Ba(2)–O(62)	81.21(12)	Ba(2)–O(51)–P(52)	154.24(24)
O(51)–Ba(2)–O(73)	144.03(11)	Ba(2)–O(62)–P(63)	157.95(23)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

poses to $Cu[C(CO_2CH_3)_3]_2$ and Cu^0 when heated above 160 °C under a vacuum of 3×10^{-5}–3×10^{-4} Torr. $Ba[C(CO_2CH_3)_3]_2 \cdot 0.36THF$ (**5**) does not sublime upon being heated to 238 °C under 4×10^{-5} Torr. HMPA loss is observed when **6** is heated to 141 °C under 4.5×10^{-5} Torr. The residue is not volatile.[16]

The above data suggest that the tricarbomethoxymethanate anion does not give rise to Cu(II) complexes with enhanced volatilities as compared to other nonfluorinated β-diketonate complexes such as $Cu(acac)_2$ (acac = acetylacetonate), reported[17] to sublime at 78 °C under 0.05 Torr and the tetramer $[(thd)Cu(OCH_3)]_4$, reported[18] to sublime at 120 °C under 10^{-4} Torr. The reduced volatility imparted by the tricarbomethoxymethanate ligand combined with aggregation in the solid state accounts for the partial decomposition of **2** and **4′** to Cu^0 upon heating *in vacuo*. The reduced volatility of tricarbomethoxymethanate complexes becomes even more pronounced when the coordinated cation is Ba^{2+}, and this trend is similar to that already observed for Cu^{2+} and Ba^{2+} complexes bearing acac and thd ligands.

Thermolysis studies

Thermal decompositions of **2**, **4** and **4′** at 1000 °C, in a 20% O_2–80% Ar atmosphere for 30 min, yield CuO. Complexes **2** and **4** decompose to Cu^0 and trace amounts of Cu_2O upon heating to 1000 °C, for 30 min, under argon. Cu_2O-free copper metal is obtained when **4′** is heated to 1000 °C under the same conditions.

Thermal decomposition of **5** at 1000 °C, in a 20% O_2–80% Ar atmosphere for 30 min, gives a residue containing $BaCO_3$ as the major crystalline phase. These results are in line with those reported by Gordon *et al.* concerning the deposition of films from liquid barium β-diketonate precursors.[19] An increase in the annealing time at 1000 °C to 2 h greatly reduces the amount of $BaCO_3$ in the residue and, after 4 h at 1000 °C, only BaO and BaO_2 are detected by X-ray powder diffraction.[20] However, an analysis of the residual solid by infrared spectroscopy indicates that a small amount of $BaCO_3$ is still present.

We have also found that the thermal decomposition of **5** at 500 °C, in a 20% O_2–80% Ar atmosphere for 2 h, gave residues containing $BaCO_3$ as the only crystalline phase. This result, combined with those described above, suggests that the formation of barium oxide phases at elevated temperatures does not originate directly from the decomposition of the barium precursor but arises from the decomposition of $BaCO_3$ formed intermediately.[21]

Thermolysis of **5** at 500 and 1000 °C, in pure argon for 2 h, gave residues containing carbonaceous impurities. The sample heated to 1000 °C contained BaO as the only crystalline phase whereas that heated to 500 °C was amorphous. However, an analysis of this latter sample by infrared spectroscopy indicated that $BaCO_3$ was present. Thus, it appears from these results and those obtained under O_2–Ar that the high thermodynamic stability[22] of $BaCO_3$ is the main controlling factor in the thermolysis of **5** and that the nature of the atmosphere influences the decomposition to a lesser degree.

Thermal decomposition of **6** at 1000 °C, in pure argon for 2 h, yielded residues containing BaO and BaO_2 as the major crystalline phases accompanied by other, low-level, unidentified phases. $BaCO_3$ was not detected.

Thermolysis of **6** at 1000 °C, in a 20% O_2–80% Ar atmosphere, resulted in the formation of BaO and BaO_2 as the main crystalline products.

Conclusions

Novel Cu^{2+} and Ba^{2+} complexes bearing the tricarbomethoxymethanate anion, $^{-}C(CO_2CH_3)_3$ (L), have been prepared. Structural characterization of these complexes by single-crystal X-ray diffraction has demonstrated the versatility of L: complexes with different nuclearities may be obtained depending on whether L functions as a bidentate or a tridentate ligand. The reaction between $Cu(OCH_3)_2$ and HL, in THF, gives a mixture of two products, $CuL(OCH_3)$ and $CuL_2(THF)_2$. Available data suggest that $CuL(OCH_3)$ is polymeric in the solid state and X-ray crystallography shows $CuL_2(THF)_2$ to be a monomeric, tetragonally distorted, octahedral complex. In this complex, the THF molecules occupy the axial positions of the octahedron and are weakly coordinated to the CuL_2 moiety. In the absence of THF, a polymeric structure involving square planar $Cu(acac)_2$-type molecules is obtained; the molecules are linked to neighboring units *via* the carbonyl group of the attendant CO_2CH_3 moiety leading to a layered ladder-type structure. In the case of the larger Ba^{2+} ion, a polymeric $[BaL_2]_n$ material is formed; the polymeric structure of this material is broken up by strong Lewis bases and, upon reaction with the neutral donor ligand HMPA, the dimeric complex $(HMPA)_2(\eta^2\text{-}L)Ba(\mu\text{-}\eta^2,\eta^1\text{-}L)_2Ba(\eta^2\text{-}L)(HMPA)_2$ is isolated.

These results indicate that the tricarbomethoxymethanate ligand is effective in using the central CO_2CH_3 group as a donor ligand to a second metal when no other donors (*e.g.* THF or HMPA) are available.

$CuL_2(THF)_2$ readily loses the two coordinated THF molecules to give CuL_2, which sublimes under high vacuum. Under an O_2–Ar atmosphere, thermolysis of CuL_2 yields CuO whereas thermolysis under pure argon yields copper metal. Similar pyrolysis results are obtained for $CuL(OCH_3)$. The non-volatile $[BaL_2]_n$ compound yields $BaCO_3$ upon decomposition under O_2–Ar at 500 °C and residues containing varying amounts of BaO, BaO_2 and $BaCO_3$ are obtained upon pyrolysis at 1000 °C. It was found that extended annealing periods at 1000 °C are necessary to completely remove $BaCO_3$. Similar phases to those produced under O_2–Ar are obtained when the thermolysis of $[BaL_2]_n$ is carried out under argon, except that carbonaceous impurities are also present in the final residues. Residues containing BaO and BaO_2 are obtained upon pyrolysis of $Ba_2L_4(HMPA)_4$ at 1000 °C under argon, and similar results are obtained when the decomposition is performed under O_2–Ar.

Experimental

General considerations

Manipulations of all reactants and products were carried out under an inert atmosphere of dry (molecular sieves) nitrogen, with rigorous exclusion of air and moisture. All hydrocarbon and ethereal solvents were dried and distilled from sodium or potassium benzophenone ketyl. NMR solvents were dried over molecular sieves and kept in a helium-filled drybox. Barium granules were purchased from Johnson Matthey. Hexamethylphosphoramide (HMPA) and copper(II) methoxide were obtained from Aldrich Chemical Company, Inc. Anhydrous ammonia was purchased from Air Products. Melting points were measured on an Electrothermal melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian XL-300 spectrometer; chemical shifts were referenced to the protio impurity of the NMR solvent (^1H) or to the NMR solvent (^{13}C). Infrared spectra were recorded on a Nicolet 510P FTIR spectrometer using KBr pellets. Differential scanning calorimetry (DSC) data were obtained under a helium flow on a TA Instruments 910 Differential Scanning Calorimeter. X-Ray powder diffraction analyses were carried out on a Scintag XDS2000 diffractometer. Elemental analyses were performed by Oneida Research Services, Inc. (Whitesboro, NY).

Syntheses

$HC(CO_2CH_3)_3$ (1). Tricarbomethoxymethane, $HC(CO_2CH_3)_3$ (**1**), was prepared from the reaction between $NaCH(CO_2CH_3)_2$ and $ClCO_2CH_3$ as described in the literature.[7] ^1H NMR (300 MHz, 25 °C, DMSO-d_6): δ 3.73 (s, 9H, OCH_3), 5.07 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (75.4 MHz, 25 °C, DMSO-d_6): δ 53.0 (s, OCH_3), 57.7 (s, CH), 164.3 (s, C=O). IR (ν/cm^{-1}): 3019 (w), 2961 (m), 2849 (w), 1761 (vs), 1744 (vs), 1433 (s), 1319 (s), 1277 (s), 1200 (s), 1163 (s), 1036 (s), 1026 (s), 970 (w), 911 (m), 804 (w), 779 (w), 648 (m), 592 (w). Mp: 39–46 °C (lit.[23] 45–46 °C).

Reaction between $Cu(OCH_3)_2$ and 1. A 250 mL Schlenk flask equipped with a magnetic stirrer bar was loaded in a drybox with 0.1656 g (1.32 mmol) of $Cu(OCH_3)_2$ and 0.5021 g (2.64 mmol) of **1**. The flask was removed from the drybox and charged with 50 mL of THF *via* syringe. A blue suspension was obtained. The suspension was stirred at room temperature, under dinitrogen, for 50 h during which time it became bright green. The bright green suspension was filtered through a glass frit. A pale blue precipitate was collected on the glass frit and a green filtrate was recovered in the flask connected to the glass frit. The pale blue precipitate (**2**) was dried *in vacuo* for several days (yield = 0.2683 g). The green solution was carefully layered with hexanes and the mixture allowed to stand in a freezer at −15 °C. After 5 days, a crop of green crystals (**3**) was obtained, which was separated from the solvent mixture and dried in a stream of dinitrogen for several days (yield = 0.1422 g).

The exact nature of the pale blue solid, compound **2**, is unclear. Its insolubility in THF, at room temperature, suggests that it may be polymeric in the solid state. However, the polymeric network does not seem to be very strong since this compound dissolves readily in refluxing toluene and refluxing THF. The presence of weakly interacting polymeric chains is also suggested by the rather low melting/decomposition range of **2**: the solid first turns brown between 218 and 221 °C and then melts with decomposition between 230 and 232.5 °C. The infrared spectrum of **2** shows the following bands (ν/cm^{-1}): 2990 (w), 2953 (m), 2930 (w), 2888 (w), 2874 (w), 2816 (w), 1709 (s, sh), 1694 (s), 1622 (vs), 1497 (s), 1474 (s), 1455 (s, sh), 1437 (s, sh), 1379 (s), 1316 (s), 1291 (s), 1194 (s), 1125 (s), 1103 (vs), 1092 (s), 1044 (m), 963 (w), 816 (m), 791 (m), 777 (m), 552 (m), 484 (w), 467 (w), 409 (m), which are consistent with the presence of the $^-C(CO_2CH_3)_3$ anion. Elemental analysis for C, H, N and Cu gave the following results: C, 35.09; H, 4.36; N, 0.00; Cu, 20.84%. These results suggest the presence of only one $^-C(CO_2CH_3)_3$ anion per Cu(II) center and compare favorably with the values calculated for $Cu[C(CO_2CH_3)_3][OCH_3]$: C, 33.87; H, 4.26; N, 0.00; Cu, 22.40%. Lastly, thermal decomposition of **2** in a tube furnace, under argon, at 1000 °C, proceeds with a weight loss of 75.7% to give a rust-colored residue identified as metallic copper by X-ray powder diffraction; a weight loss of 77.6% is expected for $Cu[C(CO_2CH_3)_3][OCH_3]$.

The nature of the green crystals, compound **3**, was established *via* a single-crystal X-ray diffraction analysis. **3** is a mononuclear complex of empirical formula $Cu[C(CO_2CH_3)_3]_2[C_4H_8O]_2$. This complex readily loses the two THF molecules bound to the Cu(II) center upon drying (see Results and discussion) to give a green amorphous powder, compound **4**. Elemental analysis of **4** for C, H, N and Cu indicates that the latter compound may be formulated as $Cu[C(CO_2CH_3)_3]_2$. Anal. calc. for $CuO_{12}C_{14}H_{18}$: C, 38.06; H, 4.11; N, 0.00; Cu, 14.38%. Found: C, 38.01; H, 4.05; N, 0.00; Cu, 14.73%. IR (ν/cm^{-1}): 3025 (w), 3007 (w), 2984 (w), 2961 (m), 2950 (m, sh), 2911 (w), 2875 (w), 2843 (w), 2342 (w), 1696 (s), 1611 (vs), 1499 (m), 1451 (vs), 1381 (vs), 1292 (s), 1264 (m), 1242 (m, sh), 1192 (s), 1112 (vs), 1098 (vs), 1022 (m), 966 (w), 915 (w), 887 (w, br), 849 (w), 812 (m), 793 (m), 781 (m), 737 (w), 666 (w, br), 519 (w), 494 (w), 471 (w), 415 (m). Mp: the solid turns brown and then melts with decomposition between 241 and 244 °C. Thermal decomposition of **4** in a tube furnace, under argon, at 1000 °C, proceeds with a weight loss of 85.1% to give a rust-colored residue identified as metallic copper by X-ray powder diffraction; a weight loss of 85.6% is calculated for $Cu[C(CO_2CH_3)_3]_2$.

Reaction between 1 and 2. A 250 mL Schlenk flask equipped with a magnetic stirrer bar was loaded in a drybox with 0.0978 g (0.51 mmol) of **1** and 0.1453 g (0.51 mmol) of **2**. The flask was removed from the drybox and charged with 100 mL of toluene *via* syringe. Under a nitrogen flow, the flask was fitted with a Dean–Stark trap. The suspension was heated to reflux with an oil bath. As the reaction mixture began to reflux, all of the pale blue solid dissolved and a dark green solution was obtained. An 82 mL portion of condensate was collected *via* the Dean–Stark trap to ensure that all of the methanol produced in the reaction had been removed and also to reduce the volume of the reaction mixture. The heating and stirring of the solution were stopped but the oil bath was kept underneath the flask. Upon slow cooling to room temperature, a crop of emerald green crystals was obtained. The crystals were isolated by removal of the supernatant with a canula and dried *in vacuo*. Yield: 0.0933 g (41%). The nature of the emerald green crystals, compound **4′**, was established *via* a single-crystal X-ray diffraction analysis. **4′** is a polymer made of $Cu[C(CO_2CH_3)_3]_2$ repeat units. Anal. calc. for $CuO_{12}C_{14}H_{18}$: C, 38.06; H, 4.11; N, 0.00; Cu, 14.38%. Found: C, 37.96; H, 4.05; N, 0.00; Cu, 14.81%. IR: the infrared spectrum of **4′** is the same as that of **4**. Mp: the solid turns brown and then melts with decomposition between 230 and 240 °C.

$Ba[C(CO_2CH_3)_3]_2 \cdot 0.36C_4H_8O$ (5). A 250 mL Schlenk flask equipped with a magnetic stirrer bar was loaded in a drybox with 1.6010 g (11.66 mmol) of barium granules and 4.4341 g (23.32 mmol) of **1**. The flask was removed from the drybox and charged with 100 mL of THF *via* syringe. The ligand dissolved readily, producing a clear and colorless solution. No reaction was observed between barium and **1** upon stirring the mixture for several minutes. Ammonia was bubbled into the solution for 15 min. A large amount of a white precipitate formed and moderate gas evolution was observed. The reaction mixture was stirred for 49 h under a slow purge (1 bubble per 10 s) of $NH_{3(g)}$, during which time all of the barium was consumed. During the reaction period, further activation with $NH_{3(g)}$ and addition of solvent to return to the original volume were necessary. At the end of the reaction, a vigorous stream of $NH_{3(g)}$ was passed through the solution for 5 min to ensure that all of the barium had reacted. A white solid was obtained upon filtration of the milky reaction mixture through a glass frit. The white solid was washed with two 50 mL portions of THF and dried *in vacuo* for 48 h. The reaction product, $Ba[C(CO_2CH_3)_3]_2 \cdot 0.36\,C_4H_8O$, was obtained in 99% yield. Anal. calc. for $BaO_{12}C_{14}H_{18} \cdot 0.36C_4H_8O$: C, 34.24; H, 3.89; N, 0.00%. Found: C, 34.04; H, 3.63; N, 0.27%. ^1H NMR (300 MHz, 25 °C, DMSO-d_6): δ 1.74 (m, 1.44H, THF), 3.41 (s, 18H, OCH_3), 3.59 (m, 1.44H, THF). $^{13}C\{^1H\}$ NMR (75.4 MHz, 25 °C, DMSO-d_6): δ 25.1 (s, THF), 49.5 (s, OCH_3), 67.0 (s, THF), 76.3 (s, deprotonated carbon), 169.5 (s, C=O). IR (ν/cm^{-1}): 2986 (w), 2950 (m), 2851 (w), 1684 (vs), 1622 (vs), 1557 (s), 1439 (vs), 1358 (vs), 1300 (m), 1258 (m), 1188 (m), 1084 (vs), 966 (w), 901 (w), 806 (m), 766 (w), 604 (w, br), 438 (w, br). Mp: 273–281 °C (dec.).

$Ba_2[C(CO_2CH_3)_3]_4[OP(N(CH_3)_2)_3]_4$ (6). A 100 mL Schlenk flask equipped with a magnetic stirrer bar was loaded in a drybox with 0.2996 g (0.55 mmol) of **5**. The flask was removed from the drybox and charged with 50 mL of toluene and 5 mL (28.74 mmol) of HMPA. The Schlenk flask was fitted with a condenser and the suspension heated to reflux under an inert atmosphere of dinitrogen. As the reaction mixture began to reflux, all of the solid dissolved. The solution was refluxed for 1 h and then allowed to cool to room temperature. The toluene was removed *in vacuo*, leaving a small amount of a clear and colorless solution (HMPA) in the flask. A 150 mL portion of *n*-pentane was added to the HMPA solution, whereupon a white suspension, made up of very fine particles, and a sticky grease-like solid were obtained. The mixture was cooled in a freezer at −15 °C for 6 days, during which time the grease-like solid turned into clear and colorless needles. The needles were crushed with a spatula and the solid was collected *via* filtration of the suspension through a glass frit. The white solid was washed with 25 mL of *n*-pentane and dried *in vacuo* for 20 h. The reaction product, $Ba_2[C(CO_2CH_3)_3]_4[OP(N(CH_3)_2)_3]_4$ (**6**), was obtained in 80% yield. Anal. calc. for $Ba_2P_4O_{28}N_{12}C_{52}H_{108}$: C, 35.73; H, 6.23; N, 9.62; P, 7.09%. Found: C, 35.74; H, 5.85; N, 9.33; P, 6.78%. ^1H NMR (300 MHz, 25 °C, DMSO-d_6): δ 2.53 [d, $^3J(^1H, ^{31}P) = 9.6$ Hz, 18H, HMPA], 3.42 (s, 9H, OCH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, 25 °C, DMSO-d_6): δ 36.4 [d, $^2J(^{13}C, ^{31}P) = 2.9$ Hz, HMPA], 49.4 (s, OCH_3), 76.2 (s, deprotonated carbon), 169.3 (s, C=O). IR (ν/cm^{-1}): 2994 (m), 2944 (s), 2896 (s), 2847 (m), 2805 (m), 1678 (vs), 1642 (vs), 1568 (s), 1439 (vs), 1356 (vs), 1298 (vs), 1238 (s), 1186 (vs), 1084 (vs), 986 (vs), 897 (w), 806 (m), 750 (s), 482 (m). Mp: the solid first undergoes a solid state transformation between 71 and 78 °C (the material shrinks) and then melts between 118 and 138 °C.

Crystal structure analyses

$Cu[C(CO_2CH_3)_3]_2[C_4H_8O]_2$ (3). Green crystals of **3** were grown from a THF–hexanes solution cooled to −15 °C. A crystal with approximate dimensions 0.12 × 0.32 × 0.40 mm was mounted using silicone grease and transferred to a goniostat, where it was cooled to −170 °C for characterization and data collection.[24] Crystals of **3** lose their crystallinity fairly rapidly when allowed to stand in air at room temperature but are quite stable once in a cold stream of nitrogen. Four standards measured every 300 reflections showed no significant trends. No correction was made for absorption.

The structure was solved by use of a combination of direct methods (MULTAN78) and Fourier techniques. The coordinates of the copper atom and 13 of the carbon and oxygen atoms were obtained from an initial E-map. The positions of the remaining atoms, including all of the hydrogens, were obtained from subsequent least-squares refinements and difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. The final difference map was featureless, the highest peak being 0.4 e Å^{-3} and the minimum negative peak −0.5 e Å^{-3}.

Crystal data and additional details of data collection and refinement are given in Table 4. Selected bond lengths and angles are shown in Table 1.

$Cu[C(CO_2CH_3)_3]_2$ (4′). Emerald green crystals of **4′** were obtained *via* slow cooling of a hot concentrated toluene solution of this complex. A crystal with approximate dimensions 0.25 × 0.25 × 0.30 mm was mounted using silicone grease and transferred to a goniostat, where it was cooled to −122 °C for characterization and data collection.[24] A lower temperature was not used for data collection as the compound appeared to undergo a phase transition below −122 °C. Four standards measured every 300 reflections showed no significant trends. No correction was made for absorption.

The structure was solved by use of a combination of direct methods (MULTAN78) and Fourier techniques. The coordinates of all of the non-hydrogen atoms were obtained from an initial E-map. The positions of the hydrogen atoms were obtained from subsequent least-squares refinements and difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. The final difference map was featureless, the highest peak being 0.34 e Å^{-3} and the minimum negative peak −0.24 e Å^{-3}.

Crystal data and additional details of data collection and refinement are given in Table 4. Selected bond lengths and angles are shown in Table 2.

$Ba_2[C(CO_2CH_3)_3]_4[OP(N(CH_3)_2)_3]_4$ (6). Large colorless crystals of **6** were grown from an HMPA–*n*-pentane solution

Table 4 Crystallographic data for $Cu[C(CO_2Me)_3]_2[THF]_2$ (**3**), $Cu[C(CO_2Me)_3]_2$ (**4′**) and $Ba_2[C(CO_2Me)_3]_4[HMPA]_4$ (**6**)

	3	**4′**	**6**
Empirical formula	$C_{22}H_{34}CuO_{14}$	$C_{14}H_{18}CuO_{12}$	$C_{52}H_{108}N_{12}O_{28}Ba_2P_4$
Formula weight	586.05	441.84	1748.06
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	7.518(1)	6.6222(8)	16.327(2)
b/Å	9.620(1)	10.5537(13)	24.327(3)
c/Å	18.043(3)	13.2204(17)	10.680(1)
α/°			100.26(1)
β/°	93.72(1)	102.718(7)	99.66(1)
γ/°			72.55(1)
U/Å^3	1302.23	901.29	3952.40
μ(Mo-Kα)/cm^{-1}	9.044	12.721	11.457
Z	2	2	2
T/°C	−170	−122	−150
2θ range/°	6.0–55.0	6.0–55.0	6.0–45.0
Reflns collected	4734	4457	11 117
Unique reflns	3000	2081	10 389
R_{int}	0.022	0.019	0.027
Obsd reflns [$F > n\sigma(F)$]	2505 (n = 3)	1803 (n = 3)	8654 (n = 2.33)
R, R_w[a] (obsd reflns)	0.0365, 0.0385	0.0272, 0.0283	0.0436, 0.0478

[a] $R = \sum \| F_o | - | F_c \| / \sum | F_o |$; $R_w = [\sum w(| F_o | - | F_c |)^2 / \sum w | F_o |^2]^{1/2}$ where $w = 1/\sigma^2(| F_o |)$.

cooled to −15 °C. A fragment with approximate dimensions 0.25 × 0.25 × 0.25 mm was cleaved from a large crystal in a nitrogen-filled glovebag. The crystal was affixed to a glass fiber with silicone grease and transferred to a goniostat, where it was cooled to −150 °C for characterization and data collection.[24] Four standards collected every 300 reflections showed no significant variation in intensity. No correction was made for absorption.

The structure was solved by use of a combination of direct methods (SHELXS-86) and Fourier techniques. The locations of the Ba atoms of the two independent half-molecules were determined from an initial E-map and the remaining non-hydrogen atoms located in successive difference Fourier syntheses. Hydrogen atoms were included in the refinements but fixed at idealized positions. The final blocked least-squares refinement was completed using anisotropic thermal parameters for all non-hydrogen atoms and fixed positions and isotropic thermal parameters for all hydrogens. The final difference map was essentially featureless with the largest peaks (<1.3 e Å^{-3}) located in the immediate vicinity of the barium atoms.

Crystal data and additional details of data collection and refinement are given in Table 4. Selected bond lengths and angles are shown in Table 3.

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