Synthesis and thermolytic behavior of tin(IV) formates: in search of recyclable metal-hydride systems[†]

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The synthesis and characterization of the series of organotin formates together with their thermolytic behavior are described. The diformate $Bu_2^n Sn \{OC(O)H\}_2$ (1) was synthesized by the reaction of $Bu^{n}_{2}SnH_{2}$ with formic acid. The triorganotin monoformate compounds $R_{3}SnOC(O)H$ (R = Cy (cyclohexyl)) 3, Mes, (mesityl, 2,4,6-trimethylphenyl) 4, and Dmp (2,6-dimethylphenyl 5) were obtained by the reaction of R₃SnOH with formic acid. Their X-ray crystal structures along with that of the previously reported formate $(PhCH_2)$, SnOC(O)H(2) were determined. The diformate 1 exhibits an extended two-dimensional polymeric structure in which six-coordinate tin centers are linked by formate bridges. The tribenzyltin formate (2) possesses a chain structure in which the five-coordinate $Sn(CH_2Ph)_3$ units are bridged by formate ions. The cyclohexyl derivative 3 was observed to have a similar structure. In contrast, the Mes and Dmp derivatives 4 and 5 support monomeric structures in which the four-coordinate tin atom is bound to an oxygen of the formate ligand. Heating the compounds in various high boiling solvents produced no decomposition up to 120 °C in the case of 1 and refluxing a solution of 2 or 3 in mesitylene or diglyme left the starting material mostly unchanged, although 3 decomposed to an insoluble orange solid in refluxing decalin. In contrast, the heating of 4 and 5 in refluxing mesitylene led to elimination of CO to give the tin hydroxides. The results are in contrast to the known thermolytic behavior of R_3 SnOC(O)H (R = Prⁿ or Buⁿ) complexes, which eliminate CO₂ to generate R₃SnH. Compounds 3-5 are rare examples of structurally characterized tin formates.

Introduction

A necessary requirement for a hydrogen (H₂) based economy, especially for use in the transportation sector, is its storage for controlled delivery, presumably to a fuel cell.¹⁻⁵ Chemical hydrides for hydrogen storage are typically composed of lighter elements, resulting in higher gravimetric storage capacities, making these attractive as H₂ carriers. Due to its high gravimetric capacity of H₂ (19.6 wt%) and low molecular weight (30.7 g mol⁻¹), chemical hydrogen storage research has been dominated by one material in particular, ammonia borane (H₃N–BH₃, AB).⁶⁻¹⁵

The practical viability of any chemical H_2 storage system is dependent on efficient recyclability of the energy carrier. This means that once AB is dehydrogenated the resulting "spent fuel" should ideally be regenerated in order to reform the original B– H bonds contained within the borane fragment. Depending on the nature of the H_2 carrier material, a variety of regeneration schemes could be envisioned. We recently described such a cycle utilizing tin hydrides as reductants towards the regeneration of AB, starting from polyborazylene (PB).⁹ In order to increase overall process efficiencies, recycling of the tin-containing reductant would also be useful.¹¹ In addition, regenerable metalhydride systems would be of general practical utility *via* (a) reduction in quantities of metal wastes; (b) reducing disposal costs and (c) reducing the negative impact of heavy metals in the environment.

Reagents containing hydridic hydrogen atoms are usually produced under either harsh or energy intensive conditions,¹⁶ neither of which is desirable for large scale applications. One class of compounds that have the potential to be used in a recyclable hydride system are metal formates.¹¹ Carbon dioxide (CO₂) can add across metal-hydride bonds to form a metal formate moiety, *e.g.* in the case of the ketiminatoaluminium hydride AlH(OCMeCHCMeNAr)₂ (Ar = 2,6-Prⁱ₂-C₆H₃).¹⁷ Formate complexes can also be synthesized *via* metathesis reactions between metal halides and alkali metal formates.¹⁸

Formates have multiple potential decomposition pathways available to them during thermolysis.¹⁹ It has been shown that under thermolytic conditions, the tripropyl and tributyl tin formates (R_3 SnOC(O)H, $R = Pr^n$, Bu^n) release CO₂, yielding tin hydrides.²⁰ This process is reversible for Bun₃SnOC(O)H.²¹ One common potential side reaction that can occur when metal formates are subjected to elevated temperatures is the elimination of CO to yield metal hydroxides. As a possible methodology for metal-based reductant recycle (so that these could be used in AB spent fuel regeneration chemistries), we therefore sought to investigate the conditions for tin hydride generation via thermolysis reactions of tin(IV) formates. We also sought to synthesize the formate compounds from the corresponding tin halide and formic acid. Formic acid itself can be synthesized from H_2 and CO_2 ,²² which results in the overall catalytic cycle shown in Scheme 1. Only a limited number of tin formates are known, and only a handful of these been structurally characterized. These include

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 $\label{eq:Scheme 1} Scheme 1 \quad Proposed \ catalytic \ cycle \ for \ the \ regeneration \ of \ Sn(tv) \ hydrides.$

the triphenyl derivative Ph₃SnOC(O)H,²³ which has an oligomeric structure with penta-coordinated tin atoms. KSn(OC(O)H)₃,²⁴ a three dimensional polymer, Me₂Sn{OC(O)H},²⁵ which has a two-dimensional sheet structure, and the monomeric Sn(II) derivative HC{C(Me)N(C₆H-2,6-Prⁱ₂)}_2SnOC(O)H.²⁶

Experimental

General

Chemicals were purchased from either Aldrich or Acros and used as received. Buⁿ₂SnH₂,²⁷ (PhCH₂)₃SnCl,²⁸ (PhCH₂)₃SnOC(O)H,²⁹ Cy₃SnOH³⁰ and Mes₃SnOH³¹ were prepared by published methods. NMR spectra were recorded on INOVA 600 MHz spectrometers and were referenced internally to residual protio-solvent for the ¹H and ¹³C or externally to SnMe₄ for the ¹¹⁹Sn nuclei. The ¹¹⁹Sn{¹H} chemical shift of (PhCH₂)₃SnOC(O)H, δ –38.8, was not reported previously.

$Bu^{n}_{2}Sn{OC(O)H}_{2}$ (1)

Diethyl ether (*ca.* 15 mL) was added to a flask containing Buⁿ₂SnH₂ (2.428 g, 10.33 mmol). With rapid stirring, HC(O)OH (0.8 mL, 20.67 mmol) was added dropwise to the colourless solution. Within 30 min of the addition effervescence of H₂ was observed. The solution stirred overnight and then the volatiles were removed by evaporation under reduced pressure. The product was crystallized by sublimation under reduced pressure. Yield: 2.403 g (72%). Mp 86–89 °C. Calcd for C₁₀H₂₀O₄Sn: C, 37.19; H, 6.24. Found: C, 38.19, H, 6.80. ¹¹⁹Sn{¹H} NMR (C₆D₆) δ : -14.1. ¹³C{¹H} NMR (C₆D₆) δ : 12.2 (s), 24.0 (s), 25.1 (s), 25.5 (s) 169.5 (s). ¹H NMR (C₆D₆) δ : 0.78 (t, ³J_{HH} = 7.2 Hz, 6H), 0.89 (t, ³J_{HH} = 7.2 Hz, 4H), 1.22 (m, 4H), 1.50 (m, 4H), 8.13 (s, 2H).

Cy₃SnOC(O)H (3)

Toluene (*ca.* 20 mL) was added to a flask containing Cy₃SnOH (0.520 g, 1.35 mmol). The slurry was gently heated until all of the Cy₃SnOH had dissolved. With rapid stirring, HC(O)OH (0.5 mL, 13.25 mmol) was added dropwise to the colorless solution. A colorless precipitate immediately formed which then redissolved. The solution was stirred overnight and the volatiles were removed by evaporation under reduced pressure. The product was crystallized from chloroform by slow evaporation of the solvent. Yield: 0.489 g (88%). Mp 159–165 °C. Calcd for C₁₉H₃₄O₂Sn: C, 51.27; H, 7.70. Found: C, 50.59; H, 7.79. ¹¹⁹Sn{¹H} NMR (CDCl₃) δ : 30.8 (s). ¹³C{¹H} NMR (CDCl₃) δ : 27.0 (s), 29.1 (s), 31.2 (s), 34.2 (s), 166.4

(s). ¹H NMR (CDCl₃) δ: 1.35 (m, 3H), 1.68 (m, 5H), 1.94 (m, 3H), 8.31 (s, 1H).

Mes₃SnOC(O)H (4)

Benzene (*ca.* 60 mL) was added to a flask containing Mes₃SnOH (2.672 g, 5.42 mmol). With rapid stirring, HC(O)OH (0.5 mL, 13.25 mmol) was added dropwise to the colorless solution, which became slightly cloudy. The solution stirred overnight and the volatiles were removed by evaporation under reduced pressure. The product was crystallized from benzene by slow evaporation of the solvent. Yield: 2.513 g (89%). Mp 119–120 °C ¹¹⁹Sn{¹H} NMR (C₆D₆) δ : –121.3 (s). ¹³C{¹H} NMR (C₆D₆) δ : 21.1 (s), 24.7 (s), 129.4 (s), 139.5 (s), 142.1 (s), 144.2 (s), 164.4 (s). ¹H NMR (C₆D₆) δ : 2.02 (s, 3H), 2.42 (s, 6H), 6.68 (s, 2H), 8.22 (s, 1H).

Dmp₃SnOH

2-Bromo-1,3-dimethylbenzene (10.000 g, 54.04 mmol, 3.5 equiv.) was added dropwise to a flask containing Mg (1.445 g, 59.44 mmol, 3.85 equiv.) and thf (ca. 100 mL). The mixture was heated and maintained at reflux conditions for 19 h. The resultant orange/brown solution was cooled to room temperature and was added dropwise to a cooled (0 °C) flask containing SnCl₄ (1.8 mL, 15.44 mmol, 1 equiv.) and benzene (ca. 100 mL). A colorless precipitate formed. The mixture was refluxed for 5 h. The resultant mixture was filtered through Celite and washed with 10% aq. HCl. The volatile fractions were removed by evaporation under reduced pressure. The crude oil that remained was dissolved in toluene (ca. 100 mL) and poured into 15% aq. NaOH (ca. 150 mL). This mixture was refluxed for 18 h and cooled to room temperature. The layers were separated and the aqueous layer was extracted with three 50 mL portions of diethyl ether. The ethereal extracts were combined with the original toluene layer and dried over anhydrous Na₂SO₄. The volatiles were removed by evaporation under reduced pressure and the product was crystallized from benzene by slow evaporation of the solvent. Yield: 5.015 g (72%). Mp 138–140 °C. Calcd for C₂₄H₂₈SnO: C, 63.88; H, 6.25. Found: C, 62.14; H, 6.05. ¹¹⁹Sn{¹H} NMR (C₆D₆) δ : -114.6 (s). ¹³C{¹H} NMR (C₆D₆) δ : 24.8 (s), 130.0 (s), 144.2 (s), 144.6 (s), 145.6 (s), 164.4 (s). ¹H NMR $(C_6 D_6) \delta$: 2.40 (s, 6H), 6.90 (d, ${}^{3}J_{HH} = 7.5, 2H$), 7.06 (t, ${}^{3}J_{HH} = 7.2$ Hz, 1H).

Dmp₃SnOC(O)H (5)

Benzene (*ca.* 20 mL) was added to a flask containing Dmp₃SnOH (0.933 g, 2.07 mmol). With rapid stirring, HC(O)OH (0.5 mL, 13.25 mmol) was added dropwise to the colorless solution, which became slightly cloudy. The solution was stirred overnight and the volatiles were removed by evaporation under reduced pressure. The product was crystallized from benzene by slow evaporation of the solvent. Yield: 0.927 g (94%). Calcd for $C_{25}H_{28}O_2Sn: C, 62.66;$ H, 5.89. Found: C, 62.15; H, 6.01. Mp 159–161 °C ¹¹⁹Sn{¹H} NMR (C₆D₆) δ : –131.4 (s). ¹³C{¹H} NMR (C₆D₆) δ : 2.5.0 (s), 130.3 (s), 144.3 (s), 144.8 (s), 146.0 (s). ¹H NMR (C₆D₆) δ : 2.37 (s, 6H), 6.83 (d, ³J_{HH} = 7.2 Hz, 2H), 6.99 (t, ³J_{HH} = 7.2 Hz, 1H), 8.13 (s, 1H).

X-Ray crystallography

Suitable crystals were selected and covered with a layer of hydrocarbon oil under a flow of dry nitrogen. They were mounted

Compound	1	2	$4 \cdot C_6 H_6$	5
Formula	$[C_{10}H_{20}O_4Sn]_6$	$C_{22}H_{22}O_2Sn$	$C_{31}H_{37}O_2Sn$	$C_{25}H_{28}O_2Sn$
FW	1937.70	437.09	560.30	479.16
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\overline{1}$	$P2_1/c$	$P\overline{1}$	C2/c
a/Å	11.0023(10)	11.5721(6)	8.6013(7)	32.550(5)
b/Å	15.0429(14)	15.8683(9)	16.5717(13)	7.7354(13)
c/Å	25.678(2)	10.6892(6)	18.8491(15)	23.036(4)
α (°)	101.3680(10)	90	80.2110(10)	90
β (°)	102.0150(10)	103.4760(10)	84.3680(10)	132.147(2)
γ (°)	100.9650(10)	90	89.5200(10)	90
$V/Å^3$	3955.0(6)	1908.81(18)	2634.7(4)	4300.4(12)
Ζ	2	4	4	8
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.627	1.521	1.413	1.480
μ/mm^{-1}	1.932	1.350	0.995	1.205
θ range/°	0.84 to 25.25	1.81 to 27.50	1.10 to 27.50	1.69 to 27.49
GOF on F^2	1.080	1.056	1.104	1.352
Final R indices	$R_1 = 0.0413$	$R_1 = 0.0168$	$R_1 = 0.0439$	$R_1 = 0.0377$
$[I > 2\sigma(I)]$	$wR_2 = 0.1021$	$wR_2 = 0.0402$	$wR_2 = 0.1084$	$wR_2 = 0.1061$
Maximum peak and hole/e $Å^{-3}$	2.303 and -1.466	0.488 and -0.234	3.664 and -1.022	1.684 and -1.175

 Table 1
 Selected crystallographic data and collection parameters for 1, 2, 4 and 5

on a glass fiber attached to a copper pin and placed in the cold N₂ stream on the diffractometer. X-ray data were collected on a Bruker SMART 1000 diffractometer at 90(2) K using Mo-K α radiation ($\lambda = 0.71073$ Å) see Table 1. Absorption corrections were applied using SADABS.³² The structures were solved using direct methods and refined by the full-matrix least-squared procedures in SHELX.³³ All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included in the refinement using a riding model.

Results and discussion

The reaction between dibutyltin dihydride and formic acid yielded dibutyltin diformate $Bu^{n}_{2}Sn\{OC(O)H\}_{2}$, **1**, with concomitant release of H_{2} gas. The colourless solid was heated to 120 °C under dynamic vacuum in an attempt to effect CO₂ release; however this resulted in sublimation of the tin diformate, whose structure was confirmed by X-ray crystallography. The molecular structure of **1** is shown in Fig. 1. There are six dibutyltin diformate molecules in the asymmetric unit, which exhibits an extended 2-D polymeric structure with each formate moiety bridging two tin atoms. The

Fig. 1 Molecular structure of **1** with thermal ellipsoids presented at a 30% probability level. Hydrogen atoms are not shown.

which is a sheet polymer with linear Me₂Sn moieties bridged by formate anions that produces an octahedral geometry at tin. The Sn–O bonds in 1 display a wider range of Sn–O bonds lengths (from 2.137(4) to 2.413(4) Å) than that in $Me_2Sn\{OC(O)H\}_2$ but the average Sn–O distance of 2.258 Å in 1 is very similar to the 2.246(2) Å in Me₂Sn{OC(O)H}₂.²⁴ These correspond to a delocalized π system across the C–O bonds in each bridging formate unit. The formate groups are bound to the tin atoms in a distorted square planar SnO4 arrangement. The metrical parameters of the butyl groups are in themselves unremarkable. Further attempts at heating 1 under nitrogen or in a toluene solution resulted in recovery of the tin diformate with no evidence of any decomposition product. The generation of Buⁿ₂SnH₂ from 1 requires breaking four Sn–O bonds, which may account for the difficulty in effecting thermal decomposition products at moderate temperatures. In order to obtain more facile elimination of CO₂ we focused on formates that possessed monomeric structures and lower coordination numbers at tin.

sheet structure bears a resemblance to that of Me₂Sn{OC(O)H}₂²⁴

The first compound investigated was tribenzyltin formate, (PhCH₂)₃SnOC(O)H, 2, which was prepared via a dehydration reaction between bis(tribenyltin)oxide and formic acid, as previously described.23,29 This compound crystallizes with one molecule in the asymmetric unit; however, the solid-state structure is polymeric and is composed of chains in which the tribenzyl tin moieties are linked by formate ions that symmetrically bridge the tin atoms. The structural motif is similar to the solid-state structure of the phenyl derivative.²³ The molecular structure of 2 is shown in Fig. 2 and the extended polymeric structure is shown in Fig. 3. It can be seen that the tin atoms are five-coordinate with almost equal Sn-O bonds of 2.2596(11) and 2.2700(11) Å. The symmetric bridging may be compared with that in the triphenyl tin formate analogue which has Sn-O distances of 2.219(6), 2.317(6) and 3.372(6) Å. The three atoms form an almost linear array with an O-Sn-O angle of 171.08(4)°, similar to the triphenyltin formate structure.²³ The bridging formate moieties have indistinguishable C-O bond lengths implying complete π -electron delocalization within the formate CO₂ array.



Fig. 2 Molecular structure of 2 with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms (except those on the formate group) are not shown. Selected bond lengths (Å) and angles (°): Sn1-O1 2.2700(11), Sn1-O2A 2.2596(11), O1-C1 1.256(2), O2-C1A 1.256(2), Sn1-O1-C1 122.40(11), Sn1-O2A-C1A 122.54(1), O2-C1-O1A 125.30(15), O1-Sn1-O2A 171.08(4).



Fig. 3 Schematic representation of the extended polymeric structure of 2.

Compound 2 was heated in refluxing mesitylene (bp 163–166 °C) or diglyme (bp 162 °C) for 24 h. The solvents were evaporated under reduced pressure and the resulting material was analyzed by multi-nuclear NMR spectroscopy for the formation of either the tin hydride or tin hydroxide. NMR spectroscopy of the material, however, only contained signals attributable to tribenzyltin formate. This prompted us to investigate tin formates with bulkier substituents that would favor monomers and help facilitate tin hydride formation.

The more crowded tricyclohexyltin formate derivative Cy₃SnOC(O)H, **3**, was synthesized in a dehydration reaction *via* treatment of the tin hydroxide with formic acid. The crystals obtained from crystallization from chloroform were of poor quality and only a crude structure could be determined from the X-ray diffraction data. Attempts to grow crystals from benzene, hexanes and toluene were unsuccessful. The compound possesses a solid-state structure similar to the benzyl derivative with polymeric chains, as was previously predicted.²³ The tin center is nearly colinear with the oxygen atoms of the bridging formate moieties (O–Sn–O 172.9(7)°) and the formate groups are again symmetrically bound to the tin centers (2.30(2) and 2.34(2) Å).

Compound **3** was heated under reflux in either mesitylene, diglyme or decalin (bp 189–91 °C) for 8 h. The products obtained after evaporation of the volatile materials were analyzed by multinuclear NMR spectroscopy. Whereas the compounds that were heated in mesitylene and diglyme did not exhibit signals in their NMR spectra that were not attributable to the tin formate, the sample of **3** that was heated in decalin had decomposed into an insoluble orange compound and multiple tin-containing products (based on ¹¹⁹Sn NMR spectroscopy). None of the products could be shown to contain a Sn–H bond.

A further increase in steric hindrance is afforded by use of the mesityl or the related 2,6-dimethylphenyl (Dmp) substituents in Mes₃SnOC(O)H, 4, and Dmp₃SnOC(O)H, 5. Trimesityltin formate 4 was synthesized from Mes₃SnOH and formic acid. The isolated crystals were of suitable quality for a single crystal Xray diffraction study. This compound crystallized as a monomer with two nearly identical independent molecules in the asymmetric unit. The molecular structure of one of the independent molecules of 4 is shown in Fig. 4. This represents the first structurally characterized monomeric organotin formate complex. The coordination geometry at the tin centers is distorted tetrahedral and there are no close contacts between neighboring molecules. The Sn-O distances of 2.066(3) and 2.070(3) Å are shorter than in the bridging tin formates and the C-O distances of 1.319(6) and 1.314(6) A of the coordinated oxygen is longer as expected with the localization of the π -electrons in the C–O_{terminal} bonds in which the C-O distances are 1.204(6) and 1.216(6) Å.



Fig. 4 Molecular structure of one of the molecules in the asymmetric unit of **4** with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms (except those on the formate group) and the co-crystallized benzene molecule are not shown. Selected bond lengths (Å) and angles (°), values in brackets correspond to the second independent molecule: Sn1–O1 2.066(3) [2.070(3)], O1–C1 1.319(6) [1.314(6)], C1–O2 1.204(6) [1.216(6)], Sn1–O1–C1 125.9(3) [124.7(3)], O1–C1–O2 123.5(5) [124.4(4)].

Compound 4 was heated in refluxing mesitylene for 24 h; however the species isolated was identified as starting material. 4 was then heated in decalin at reflux for 8 h and a mixture of two compounds was obtained which were identified by ¹¹⁹Sn NMR spectroscopy as the starting material ($\delta = -121$ ppm) and trimesityltin hydroxide ($\delta = 108$ ppm). We concluded that the decomposition pathway where CO is eliminated is preferred to the CO₂ elimination route under these particular experimental conditions.

The related tris(2,6-dimethylphenyl)tin formate **5** was synthesized similarly by treating Dmp_3SnOH with formic acid. This compound also crystallizes as a monomer; however there is only one molecule in the asymmetric unit. The molecular structure of **5** is shown in Fig. 5. The coordination geometry at the tin center is also distorted tetrahedral similar to **4**. The pertinent bond lengths are indistinguishable from the mesityl-substituted derivative, although there are small differences in the angles. The only notable structural difference is that the torsion angle for Sn1O1C1O2 moiety is $-11.7(9)^{\circ}$, while in the mesityl structure **4** the corresponding angles are -169.1(4) and $-169.5(4)^{\circ}$.

Fig. 5 Molecular structure of **5** with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms (except on the formate group) are not shown. Selected bond lengths (Å) and angles (°): Sn1–O1 2.063(3), O1–C1 1.310(5), C1–O2 1.201(6), Sn1–O1–C1 121.2(3), O1–C1–O2 126.7(4).

Compound 5 was heated in mesitylene under reflux for 24 h. Analysis of the product after evaporation of the volatile components indicated that only unreacted tin formate was present. A sample of 5 was heated for 24 h in refluxing decalin. Multinuclear NMR spectroscopy of the resulting isolated product indicated complete conversion to the tin hydroxide Dmp₃SnOH (119 Sn{ 1 H}NMR; δ –114.6) with CO₂ elimination.

The ¹¹⁹Sn{¹H} NMR spectra of the compounds **4** and **5** and Dmp₃SnOH display upfield chemical shifts in the range –114.6 to –131.4 ppm. These are similar to shifts previously reported for compounds with triaryl tin(IV) moieties bound to oxygen containing ligands and are consistent with four coordinate tins.^{34,35} Compounds **1** and **3** have chemical shifts that are *ca*. 100 ppm further downfield however. This is consistent with previously noted chemical shift trends when the organic substituents are changed from aryls to alkyls.³⁵

Conclusions

Buⁿ₂Sn{OC(O)H}₂, (PhCH₂)₃SnOC(O)H and Cy₃SnOC(O)H exhibit polymeric structures in the solid-state and undergo neither CO nor CO₂ elimination decomposition pathways when exposed to prolonged heating at elevated temperatures. Mes₃SnOC(O)H and Dmp₃SnOC(O)H are the first structurally characterized examples of monomeric tin formates. Both compounds undergo CO elimination to yield tin hydroxides, contrary to the behavior reported for trialkyltin formates which eliminate CO₂ resulting in tin hydride formation. Further studies with other tin formates are currently underway to probe the factors that influence the thermal decomposition pathways of these species.

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References

- 1 T. B. Marder, Angew. Chem., Int. Ed., 2007, 46, 8116.
- 2 U. Eberle, M. Felderhoff and F. Schuth, *Angew. Chem., Int. Ed.*, 2009, **48**, 6608.
- 3 P. G. Campbell, L. N. Zakharov, D. J. Grant, D. A. Dixon and S. Y. Liu, *J. Am. Chem. Soc.*, 2010, **132**, 3289.
- 4 C. N. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.*, 2009, **38**, 279.
- 5 F. H. Stephens, V. Pons and R. T. Baker, Dalton Trans., 2007, 2613.
- 6 C. A. Jaska and I. Manners, J. Am. Chem. Soc., 2004, 126, 9776.
- 7 M. Chandra and Q. Xu;, J. Power Sources, 2006, 156, 190.
- 8 T. J. Clark, C. A. Russell and I. Manners, J. Am. Chem. Soc., 2006, 128, 9582.
- 9 B. L. Davis, D. A. Dixon, E. B. Garner, J. C. Gordon, M. H. Matus, B. Scott and F. H. Stephens, *Angew. Chem., Int. Ed.*, 2009, **48**, 6812.
- 10 S. Aldridge, A. J. Downs, C. Y. Tang, S. Parsons, M. C. Clarke, R. D. L. Johnstone, H. E. Robinson, D. W. M. Rankin and D. A. Winn, J. Am. Chem. Soc., 2009, 131, 2231.
- 11 A. D. Sutton, B. L. Davis, K. X. Bhattacharyya, B. D. Ellis, J. C. Gordon and P. P. Power, *Chem. Commun.*, 2010, 46, 148.
- 12 N. C. Smythe and J. C. Gordon, Eur. J. Inorg. Chem., 2010, 509.
- 13 A. J. M. Miller and J. E. Bercaw, Chem. Commun., 2010, 46, 1709.
- 14 P. A. Chase and D. W. Stephan, Angew. Chem., Int. Ed., 2008, 47, 7433.
- 15 B. Peng and J. Chen, Energy Environ. Sci., 2008, 1, 479.
- 16 J. Wang, A. D. Ebner and J. A. Ritter, J. Phys. Chem. C, 2007, 111, 14917.
- 17 P. C. Kuo, I. C. Chen, J. C. Chang, M. T. Lee, C. H. Hu, C. H. Hung, H. M. Lee and J. H. Huang, *Eur. J. Inorg. Chem.*, 2004, 4898.
- 18 A. A. H. Vanderzeijden, G. Vankoten, R. Luijk, K. Vrieze, C. Slob, H. Krabbendam and A. L. Spek, *Inorg. Chem.*, 1988, 27, 1014.
- 19 A. Gorski and A. Krasnicka;, J. Therm. Anal., 1987, 32, 1243.
- 20 M. Ohara and R. Okawara, J. Organomet. Chem., 1965, 3, 484.
- 21 R. J. Klingler, I. Bloom and J. W. Rathke, *Organometallics*, 1985, 4, 1893.
- 22 S. M. Ng, C. Q. Yin, C. H. Yeung, T. C. Chan and C. P. Lau, *Eur. J. Inorg. Chem.*, 2004, 1788.
- 23 K. C. Molloy, K. Quill and I. W. Nowell, J. Chem. Soc., Dalton Trans., 1987, 101.
- 24 A. Jelen and O. Lindquist, Acta Chem. Scand., 1969, 23, 3071.
- 25 F. Mistry, S. J. Rettig, J. Trotter and F. Aubke, *Acta. Cryst.*, 1990, C46, 2091.
- 26 A. Jana, H. W. Roesky, C. Schulzke and A. Döring, *Angew. Chem.*, *Int. Ed.*, 2009, 48, 1106.
- 27 A. G. Hernán, P. N. Horton, M. B. Hursthouse and J. D. Kilburn, J. Organomet. Chem., 2006, 691, 1466.
- 28 K. Sisido, Y. Takeda and Z. Kinugawa, J. Am. Chem. Soc., 1961, 83, 538.
- 29 Q. L. Xie, X. H. Xu and D. K. Zhang, Acta Chim. Sinica, 1992, 50, 508.
- 30 R. A. Howie, M. V. H. Moura, J. L. Wardell and S. Wardell, *Polyhedron*, 2004, **23**, 2331.
- 31 H. Reuter and H. Puff;, J. Organomet. Chem., 1989, 379, 223.
- 32 SADABS: Area-Detection Absorption Connection, I. Bruker AXS, Madison, WI, 1995.
- 33 SHELX and SHELXL PC: Version 5.03, I. Bruker AXS, Madison, WI, 1995.
- 34 K. C. Molloy, S. J. Blunden and R. Hill, J. Chem. Soc., Dalton Trans., 1988, 1259.
- 35 B. Wrackmeyer, Annu. Rep. NMR Spectrosc., 1999, 38, 203.

