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ORIGINAL ARTICLE

Unexpected reactivity of "GaI" towards *N*,*N*′-diaryl-β-diketiminate tin(II) chloride: Synthesis, X-ray diffraction analysis and DFT studies

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Abstract Reaction of the [HC(CMeNAr)$_2$]SnCl (Ar = 2,4,6-Me$_3$C$_6$H$_2$) with "GaI" in THF provided an unexpected transhalogenation reaction product [HC(CMeNAr)$_2$]SnI. The crystal structure shows a tin(II) ion with a distorted tetrahedral pyramidal geometry. Theoretical calculations, using density functional theory (B3LYP), suggest the probable reaction mechanism for transhalogenation. The activation energy for moving from reactant ([HC(CMeNAr)$_2$]SnCl to product [HC(CMeNAr)$_2$]SnI) is only 10.2 kcal/mol. The chloride ion is displaced by the iodine ion, probably by the help of the gallium atom when it is coordinated to the chlorine atom.

1. Introduction

We have been interested in the synthesis of tin(II) complexes stabilized by bulky ligand such as 1,8-diaminonaphthalenes (Jiménez et al., 2008), oxamides (Ibarra et al., 2012), and β-diketiminates (Muñoz et al., 2012; Rosas and Jiménez, 2012) (Fig. 1, **I–III**). The metal halides complexes (formula RSnX, where R = bulky ligand and X = halide) are considered valuable synthons in chemistry; it has been reported

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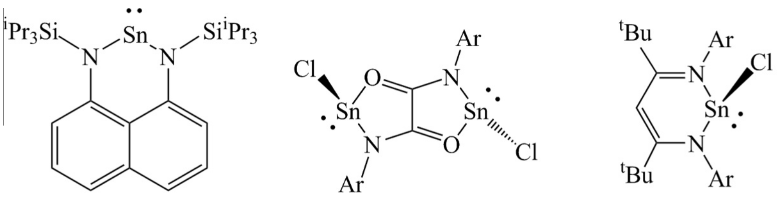

I **II**: Ar = 2,6-$^iPr_2C_6H_3$ **III**: Ar = 2,6-$^iPr_2C_6H_3$

Figure 1 Sn(II) complexes derived from bulky ligands.

the β-diketiminate Sn(II) chloride is easily replaced by alkoxide, amide, azide, triflate, and hydride (Akkari et al., 2001; Ayers and Dias, 2002; Pineda et al., 2006). However, the transhalogenation reactions on β-diketiminate Sn(II) halide has not been reported, while its germanium(II) analogue used Me_3SiF as halide source to convert the chloride to the corresponding fluoride reported by Roesky et al. (2001).

The most recent synthesis of "GaI" (Green et al., 1990) has been reported by ultrasound using gallium metal and half an equivalent of diiodine in toluene to give a pale green, where this versatile reagent has been taken an enormous importance from organic synthesis to materials chemistry (Baker and Jones, 2005). Also, the reactivity of "GaI" towards a variety of Lewis bases has been investigated. Specifically, it has been reported that "GaI" react with Sn(II) derivatives getting the transmetallation (Dias and Jin, 1996). Also, a probable reduction reaction might considered in front of M–X bonds, because it is a soft reducing agent (Lesikar and Richards, 2006). However, in this work we decide to investigate the reactivity "GaI" with $[HC(CMeNAr)_2]SnCl$ (Ar = 2,4,6-$Me_3C_6H_2$) and we obtained the unexpected transhalogenation reaction. The characterization was carried out by X-ray diffraction and the DFT calculations show the probable pathway.

2. Experimental

2.1. Material and equipment

All starting materials were purchased from Aldrich Chemical Company. Solvents were used without further purification. Melting points were determined on an Electrothermal Mel-Temp apparatus and are uncorrected. Elemental analysis was performed with the Perkin–Elmer Series II CHNS/O analyzer. The β-diketiminate Sn(II) chloride (Ayers et al., 2001) and the "GaI" (Green et al., 1990) were prepared according to published procedures.

2.2. Synthesis of compound **1**

A solution of $[HC(CMeNAr)_2]SnCl$ (Ar = 2,4,6-$Me_3C_6H_2$) (0.91 g) in toluene (30 mL) was added slowly "GaI" in toluene (10 mL) at −78 °C. The reaction mixture was warmed to room temperature, and stirring was continued for 16 h. The precipitate was filtered, and the solvent was partially reduced (ca. 20 mL). Storage of the remaining solution in a −30 °C freezer for three days afforded yellow crystals of **1** suitable for X-ray diffraction analyses. Yield (0.82 g, 71%); mp 155 °C. Anal. Calcd (%) for $C_{23}H_{29}IN_2Sn$ (579.10 g mol^{-1}): C, 47.70; H 5.05; N 4.84. Found: 47.48; H 5.11; N 4.33.

2.3. X-ray data collection and structure determination

The data for **1** and **2** were covered with a layer of hydrocarbon oil that was selected and mounted with paratone-N oil on a cryo-loop, and immediately placed in the low temperature nitrogen stream at 100(2) K. The data for **1** and **2** were recorded on a Bruker SMART APEX CCD area detector system equipped with an Oxford Cryosystems 700 Series Cryostream cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 (Sheldrick, 1990) and refined against F^2 on all data by full-matrix least-squares with SHELXL-97 (Sheldrick, 1997). Absorption corrections were applied by using SADABS. The CCDC files 1025271–1025272 contain the supplementary crystallographic data. These data can be obtained free of charge via or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK (http://www.ccdc.cam.ac.uk/conts/retrieving.html).

2.4. Theoretical calculations

The geometry of all structures was fully optimized by using the Gaussian 09 software package (Frisch et al., 2009). The B3LYP hybrid density functional (Becke, 1993), in combination with the def2-TZVP basis set (Metz et al., 2000; Peterson et al., 2003; Weigend and Ahlrichs, 2005), was adopted to calculate exchange–correlation energy since there is some rationale behind the choice of this functional. B3LYP has been used to investigate some reaction mechanisms with gallium (Ga) and tin (Sn) (Joshi and Thomson, 2005; Li et al., 2011; Liao et al., 2013; Pereira and Nascimento, 2005). Their vibrational frequencies were calculated with same level of theory in order to characterize all structures as minima or transition states. The transition state was characterized by having only one imaginary frequency with value of −65.03 and following the vibration mode of that imaginary frequency which generated the reactant (**A**) and product (**C**). The Polarizable Continuum Model (PCM) (Tomasi et al., 2005) was used to compute energies in toluene with an electrostatic dielectric constant, ε = 2.3741. This calculation is performed in the presence of a solvent by placing the solute in a cavity within the solvent reaction field via a set of overlapping spheres. All output files were visualized with the Chemcraft program v1.6.

3. Results and discussion

The reaction of $[HC(CMeNAr)_2]SnCl$ (Ar = 2,4,6-$Me_3C_6H_2$) with "GaI" in toluene provided the halide exchange product

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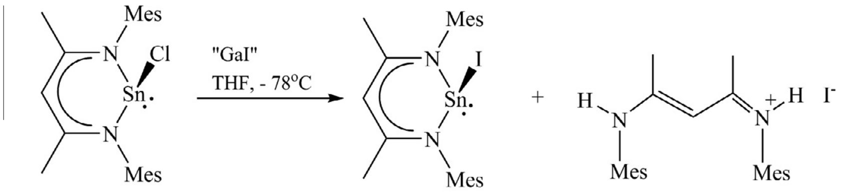

Mes = 2,4,6-$Me_3C_6H_2$

1

2

Scheme 1 Transhalogenation reaction of [HC(CMeNAr)$_2$]SnCl with "GaI".

[HC(CMeNAr)$_2$]SnI **1** (Scheme 1) as pale yellow powders that were stable under inert atmosphere and could be stored for regular periods at low temperature (−30 °C). It shows high solubility in organic solvents such as pentane, hexanes, diethyl ether, tetrahydrofuran and toluene. A suitable crystal was isolated by cooling a concentrated solution in *n*-hexane at −30 °C and its structure was determined by X-ray crystallographic analysis.

Compound **1** crystallized in the monoclinic space group *P*21/*n* as a monomer and unit cell showed two molecules which are not symmetry equivalent. Details of the X-ray crystallographic are shown in Table 1. The crystal structure shows that the metal centre (Sn) is three-coordinated and resides in a distorted tetrahedral environment with a vertex occupied by one lone electron pair (see Fig. 2). The sum of angles around the tin atom is 273.79°. The Sn–I bond length is 2.8866 (4) Å; this is in agreement with the observations to the (Sn–I 2.873 (4) Å) analogue to [HC(CMeNAr)$_2$]SnI (Ar = 2,6-iPr$_2$C$_6$H$_3$) previously reported (Jana et al., 2009). The Sn–N1 [2.177 (3)] and Sn–N2 [2.181 (3)] distances in the heterocycle corresponded with a delocalized system, while the most acute angle was associated with the bite of the chelating ligand N–Sn–N 85.51 (10)°.

Table 1 Crystalline structure data and structure refinement for **1** and **2**.

	1	2
Empirical formula	$C_{23}H_{29}IN_2Sn$	$C_{23}H_{31}IN_2$
Formula weight	579.07	462.40
Temperature, K	100(2)	100(2)
Wavelength	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*
a, Å	10.6362(8)	11.5856(5)
b, Å	11.4235(8)	13.3516(6)
c, Å	38.542(3)	14.3348(6)
α	90.00°	90.00°
β	97.875(1)°	92.7520(10)°
γ	90.00°	90.00°
V, Å^3	4638.7(6)	2214.84(17)
Z	8	4
$\rho_{calc,mg\ cm^{-3}}$	1.658	1.306
μ, mm^{-1}	2.442	1.454
2*θ* range for data collection	2.40–27.97°	2.77–28.30°
Index ranges	$-13 \leqslant h \leqslant 13$ $-14 \leqslant k \leqslant 14$ $-48 \leqslant l \leqslant 48$	$-15 \leqslant h \leqslant 15$ $-17 \leqslant k \leqslant 17$ $-18 \leqslant l \leqslant 19$
No. of reflns collected	9627	5500
No. of indep reflns	8336	5203
[R_{int}]	0.0332	0.0212
Fit goodness	1.053	1.059
R_1, wR_2 ($I > 2\sigma(I)$)	0.0400/0.0805	0.0269/0.0656
R_1, wR_2 (all data)	0.0329/0.0768	0.0253/0.0637

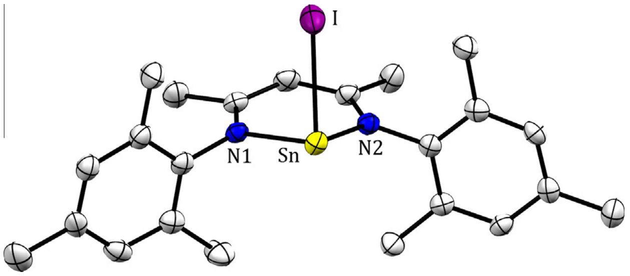

Figure 2 ORTEP drawing of compound **1** (30% probability). Hydrogens were omitted for clarity. Distances: Sn–I 2.8866 (4), Sn–N(1) 2.177 (3), Sn–N(1) 2.181 (3), N(1)–C(1) 1.336 (4), C(1)–C(2) 1.395 (4), C(2)–C(3) 1.400 (4), C(3)–N(2) 1.330 (4) Å. Bond angles: N(1)–Sn–N(2) 85.51 (10), N(1)–Sn–I 93.29 (7), N(2)–Sn–I 93.29 (7)°.

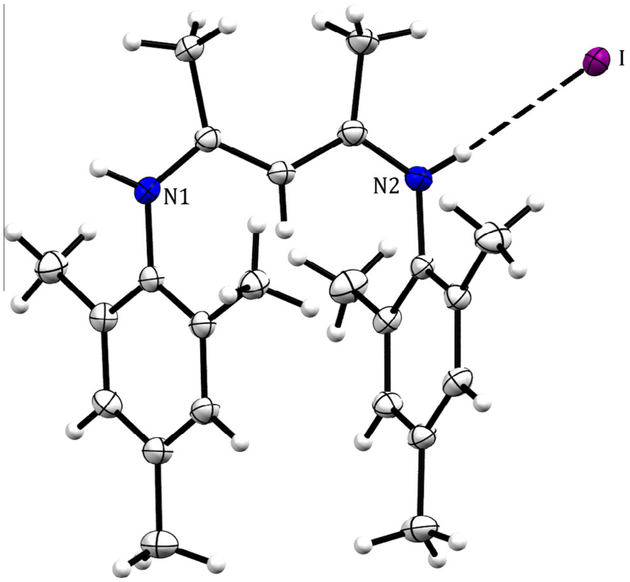

Figure 3 Molecular structure of **2** (50% probability). Distances: N(1)–C(10) 1.340 (2), N(1)–C(1) 1.437 (2), N(1)–H(1) 0.88 (2), N(2)–C(12) 1.334 (2), N(2)–C(14) 0.85(3) Å. Bond angles: C(10)–N(1)–C(1) 124.00 (14), C(10)–N(1)-H(1) 118.0 (15), C(1)–N(1)–H(1) 117.0 (14), C(12)–N(2)–C(14) 122.93 (14), C(12)–N(2)–H(2) 117.6 (17), C(14)–N(2)–H(2) 119.0 (16)°.

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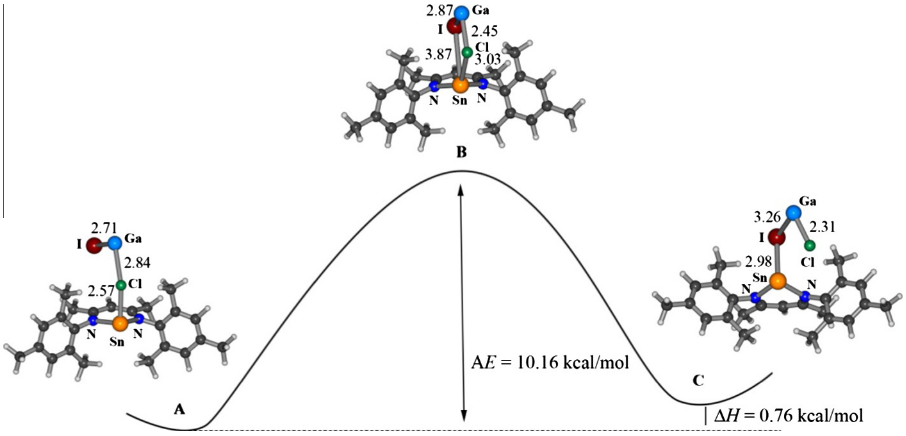

Figure 4 Potential energy surface for structures **A**, **B** and **C**. Bond lengths are given in Å.

The presence of water in the former reaction gives the β-diketiminate salt hydroiodide in a 3% yield (Scheme 1), where salt showed a W-shaped conformation (Jiménez et al., 2009). The structure of **2** was confirmed by X-ray diffraction analysis (Fig. 3). The hydrogen iodide comes from the hydrolysis reaction of the "GaI" (Eq. (1)).

$$\text{“GaI”} + 3H_2O \rightarrow Ga(OH)_3 + HI + H_2 \qquad (1)$$

Regarding the crystal structure, both amine and imine NH functionalities, N(1) and N(2), are involved in strong N(1)–H···I 2.783(3) Å, N(2)–H···I 2.819(3) Å hydrogen bonds with symmetry-related I^- ions. The network of hydrogen bonds forms a 1D supramolecular structure along the short cell axis *c*. The π···π interaction observed in the asymmetric unit, characterized by a centroid-to-centroid separation of 4.436(4) Å.

In order to explain the substitution of the chlorine atom by one iodine atom, was performed a theoretical study using density functional theory (B3LYP) in combination with the def2-TZVP basis set. Results are shown in Fig. 4. As we can observe in structure A, the gallium atom, from gallium iodide, coordinates the chlorine atom. This interaction has a value of 2.84 Å. According to experimental results, the iodine must be coordinated to the tin atom to displace the chlorine atom. We have explored the potential energy surface for this reaction and only one transition state (**B**) was found, which is shown in Fig. 4. The **B** structure is higher in energy than **A** by 10.16 kcal/mol and a four-membered heterocycle is formed. Sn–Cl and Ga–I bond lengths are significantly longer (0.46 and 0.16 Å, respectively) than those for structure **A**, and Ga–Cl bond length is much shorter by 0.36 Å. The Sn–I interaction has a value of 3.87 Å. The transition state was characterized by having only one imaginary frequency with value of −65.03 and we followed the vibration mode of that imaginary frequency which generated the reactant (**A**) and product (**C**). Structure **C** is the final product, in which the iodine atom has replaced the chlorine atom. Gallium atom is still coordinated to the iodine atom (3.26 Å). The product (**C**) has an energy difference, with respect to the first structure, of only 0.76 kcal/mol. The last energy value is almost negligible in theoretical terms. We can say that both, structure **A** and structure **B**, have almost the same stabilization energy.

In order to know the influence of the solvent on the energies of the three structures shown in Fig. 4, we carried out a study of SCRF in toluene using the polarizable continuum model (PCM). The computed energies do not vary much from the electronic energies. The AE has a slightly smaller value (9.34 kcal/mol), while the energy difference between structures **A** and **C** is 0.82 kcal/mol, **A** is still more stable than **C**. Finally, we have also analysed the zero-point energies (ZPE) and are also consistent with all previous energy, and the AE has a value of 9.16 kcal/mol and **A** is more stable than **C** by 0.69 kcal/mol.

4. Conclusions

In summary a new Sn(II) compound has been prepared by simple transhalogenation with "GaI". The reactivity of "GaI" towards β-diketiminate Sn(II)Cl was unexpected being the first time reported so far. DFT calculations suggest that transhalogenation reaction is viable and the iodine atom is capable of displacing the chlorine atom. This is possible, probably by the help of the gallium atom when it is coordinated to the chlorine atom.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2015.08.030.

References

Akkari, A., Byrne, J.J., Saur, I., Rima, G., Gornitzka, H., Barrau, J., 2001. Three coordinate divalent Group 14 element compounds with a β-diketiminate as supporting ligand L^2MX [L^2 = PhNC(Me)CHC(Me)NPh, X = Cl, I; M = Ge, Sn]. J. Organomet. Chem. 622, 190–198.

Ayers, A.E., Dias, H.V., 2002. Investigation of silver salt metathesis: preparation of cationic germanium(II) and tin(II) complexes, and

Please cite this article in press as: Ibarra-Rodríguez, M. et al., Unexpected reactivity of "GaI" towards *N,N′*-diaryl-β-diketiminate tin(II) chloride: Synthesis, X-ray diffraction analysis and DFT studies. Arabian Journal of Chemistry (2015), http://dx.doi.org/10.1016/j.arabjc.2015.08.030

silver adducts containing unsupported silver–germanium and silver–tin bonds. Inorg. Chem. 41, 3259–3268.

Ayers, A.E., Klapötke, T.M., Dias, H.V., 2001. Azido derivatives of germanium(II) and tin(II): syntheses and characterization of $[(Mes)_2DAP]GeN_3$, $[(Mes)_2DAP]SnN_3$, and the corresponding chloro analogues featuring heterocyclic six-π-electron ring systems (where $[(Mes)_2DAP] = \{N(Mes)C(Me)\}_2CH$). Inorg. Chem. 40, 1000–1005.

Baker, R.J., Jones, C., 2005. “GaI”: a versatile reagent for the synthetic chemist. Dalton Trans., 1341–1348

Becke, A.D., 1993. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 98, 5648–5652.

Dias, H.V., Jin, W., 1996. N-Methyl-2-(methylamino)troponiminate complexes of tin(II), gallium(III), and indium(III). Syntheses of $[(Me)_2ATI]_2GaI$ and $[(Me)_2ATI]_2InCl$ using the tin(II) reagent $[(Me)_2ATI]_2Sn$. Inorg. Chem. 35, 6546–6551.

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M. A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery Jr., J.A., Peralta, J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, M.J., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., Voth, G.A., Salvador, P., Dannenberg, J.J., Dapprich, S., Daniels, A.D., Farkas, Ö., Foresman, J.B., Ortiz, J. V., Cioslowski, J., Fox, D.J., 2009. Gaussian 09, Revision B.01, Gaussian Inc., Wallingford, CT.

Green, M.L.H., Mountford, P., Smout, G.J., Speel, S.R., 1990. New synthetic pathways into the organometallic chemistry of gallium. Polyhedron 9, 2763–2765.

Ibarra, R.M., Dias, H.V., Jiménez, P.V., Muñoz, F.B., Flores, P.A., Sánchez, S., 2012. Dinuclear tin(II) complex of a bulky *cis*-oxamide: synthesis, characterization, crystal structure, and DFT studies. Z. Anorg. Allg. Chem. 638, 1486–1490.

Jana, A., Roesky, H.W., Schulzke, C., Doring, T.B., Pal, A., Herbst-Irmer, R., 2009. Facile access of stable divalent tin compounds with terminal methyl, amide, fluoride, and iodide substituents. Inorg. Chem. 48, 193–197.

Jiménez, P.V., Muñoz, F.B., Roesky, H.W., Schulz, T., Pal, A., Beck, T., Yang, Z., Stalke, D., Santillán, R., Witt, M., 2008. Monomeric boron and tin(II) heterocyclic derivatives of 1,8-diaminonaphthalenes: synthesis, characterization and X-ray structures. Eur. J. Inorg. Chem. 13, 2238–2243.

Jiménez, P.V., Bernès, S., Muñoz, F.B., Kharisov, B.I., Vela, A.V., 2009. *N*-[3-(2,6-Dimethylanilino)-1-methylbut-2-enylidene]-2,6-dimethylanilinium chloride. Acta Cryst. Sect: E., o1671–o1672

Joshi, Y.V., Thomson, K.T., 2005. The roles of gallium hydride and Bronsted acidity in light alkane dehydrogenation mechanisms using Ga-exchanged HZSM-5 catalysts: a DFT pathway analysis. Catal. Today. 105, 106–121.

Lesikar, L.A., Richards, A.F., 2006. Synthesis and characterization of β-diketiminato complexes of antimony (III) halides. J. Organomet. Chem. 691, 4250–4256.

Li, B.Y., Sheu, J.H., Su, M.D., 2011. Mechanisms for the reaction of water, butadiene, and palladium complex with 1,2-dimetallacyclohexene ($R_2M = MR_2$, M = C, Si, Ge, Sn, Pb). A Theoretical Study. Organometallics 30, 4862–4872.

Liao, W.H., Ho, P.Y., Su, M.D., 2013. Mechanisms for the reactions of group 10 transition metal complexes with metal-group 14 element bonds, $Bbt(Br)E = M(PCy_3)_2$ (E = C, Si, Ge, Sn, Pb; M = Pd and Pt). Inorg. Chem. 52, 1338–1348.

Metz, B., Stoll, H., Dolg, M., 2000. Small-core multiconfiguration-Dirac–Hartree–Fock adjusted pseudopotentials for post-d main group elements: application to PbH and PbO. J. Chem. Phys. 113, 2563–2569.

Muñoz, F.B., Jiménez, P.V., Santillán, R., Hernández, F.E., López, C. S., Kharisov, B.I., 2012. Ring puckering in chloride-[N,N′-Bis(2,6-diisopropylphenyl)-2,2,6,6-tetramethylheptane-3,5-diiminato]tin (II). J. Chem. Cryst. 42, 34–37.

Pereira, M.S., Nascimento, M.A.C., 2005. Theoretical study of the dehydrogenation reaction of ethane catalyzed by zeolites containing non-framework gallium species: the 3-step mechanism × the 1-step concerted mechanism. Chem. Phys. Lett. 406, 446–451.

Peterson, K.A., Figgen, D., Goll, E., Stoll, H., Dolg, M., 2003. Systematically convergent basis sets with relativistic pseudopotentials. II. Small-core pseudopotentials and correlation consistent basis sets for the post-d group 16–18 elements. J. Chem. Phys. 119, 11113–11123.

Pineda, L.W., Jancik, V., Starke, K., Oswald, R.B., Roesky, H.W., 2006. Stable monomeric germanium(II) and tin(II) compounds with terminal hydrides. Angew. Chem., Int. Ed. 45, 2602–2605.

Roesky, H.W., Ding, Y., Hao, H., Noltemeyer, M., Schmidt, H.-G., 2001. Synthesis and structures of germanium(II) fluorides and hydrides. Organometallics 20, 4806–4811.

Rosas, G.V., Jiménez, P.V., 2012. Ring puckering in group 14 β-diketiminate chlorometallylenes is of quantum-mechanical origin. Polyhedron 42, 182–189.

Sheldrick, G.M., 1990. Phase annealing in SHELX-90: direct methods for larger structures. Acta Crystallogr. Sect: A. 46, 467–473.

Sheldrick, G.M.SHELX-97, 1997. Program for the Solution and Refinement of Crystal Structures. Universität Göttingen, Göttingen, Germany.

Tomasi, J., Mennucci, B., Cammi, R., 2005. Quantum mechanical continuum solvation models. Chem. Rev. 105, 2999–3093.

Weigend, F., Ahlrichs, R., 2005. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy. Phys. Chem. Chem. Phys. 7, 3297–3305.

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