ChemComm

Cite this: Chem. Commun., 2011, 47, 11677-11679

www.rsc.org/chemcomm

COMMUNICATION

Reactivity studies of a corrole germanium hydride complex with aldehydes, olefins and alkyl halides[†]

Huayi Fang,^a Zhen Ling,^a Penelope J. Brothers^b and Xuefeng Fu*^a

Received 16th August 2011, Accepted 19th September 2011 DOI: 10.1039/c1cc15076f

The tris(pentafluorophenyl) corrole germanium hydride complex (TPFC)Ge-H was prepared by the reduction of (TPFC)Ge-OCH₃ with NaBH₄. The reactivity of (TPFC)Ge-H with series of aldehydes, olefins and alkyl halides to produce α -hydroxy alkyl and alkyl complexes was studied.

The discoveries of facile syntheses of meso-aryl substituted corroles in 1999¹ triggered the revival of the chemistry of corroles. A variety of main group and transition metal elements were inserted into the corrole ring² and some of the complexes showed similar or superior properties to the related porphyrin complexes. Despite the broad scope of metallocorroles and the unique reactivity of porphyrin metal hydrides,³ the preparation and the reactivity of corrole metal hydrides have not yet been reported.

Transition metal hydrides play a central role in many of the most important catalytic processes including hydrogenation, hydroformylation, and related transformations. The rhodium porphyrin hydrides, (por)Rh-H, typical of late transition metal hydrides, display unique reactivity patterns towards an exceptional breadth of substrates including alkyl halides, olefins,⁴ aldehydes,^{4,5} and carbon monoxide.^{3c,4,6} However, analogous reactivity studies of main group metal hydride complexes are quite rare.⁷

Organo-germanium complexes show unique structures and fascinating chemical reactivity compared to both their lighter and heavier group 14 element congeners. Power *et al.* reported a series of novel organogermanium compounds and transition-metal hybrid organogermanium compounds.⁸ Roesky *et al.* studied the reactivity of germanium(II) hydrides stabilized by bulky β -diketiminate ligands.⁹ Fully-characterized germanium corrole complexes are limited to Ge(Cor)OH, Ge(Cor)OMe and the μ -oxo dimer [Ge(Cor)]₂O.¹⁰ The Ge(Cor)X (X = OCH₃, Cl) corroles have also been used as



precursors to prepare corrole derivatives functionalized on the ligand periphery by bromo, nitro and amino groups.^{10*a*-*c*} This article reports on the reactivity studies of germanium hydride corrole complexes with aldehydes, olefins and alkyl halides to form corrole germanium α -hydroxy alkyl and alkyl complexes (Scheme 1).

The H₃(TPFC) free base corrole and (TPFC)Ge-X (X = Cl, OH) complexes were prepared following the methods reported by Gross *et al.*^{1,10d} The labile chloro or hydroxo axial ligand was rapidly substituted by $-OCH_3$ or $-OCH_2CH_3$ at room temperature when (TPFC)Ge-X was dissolved in methanol or ethanol, respectively. After dissolution of (TPFC)Ge-OCH₃ (1) in ethanol, a new triplet and quartet (at -1.69 and -1.01 ppm) assigned to the methyl and methylene, respectively, of $-OCH_2CH_3$ in (TPFC)Ge-OCH₂CH₃ (2) appeared and the $-OCH_3$ singlet at -1.01 ppm disappeared (Table S1, ESI†). This diagnostic change in the ¹H NMR spectrum implied the quantitative formation of complex **2** *via* a ligand exchange reaction. Complex **2** was further characterized by molecular structure determination (Fig. S1, ESI†).

The (TPFC)Ge-H (3) was obtained by reduction of (TPFC)Ge-OCH₃ with NaBH₄ in methanol/benzene solution (1:30) (eqn (1)). Because of the large ring-current effect of the corrole ligand, the resonance of metal-bound hydrogen shifted upfield and appeared at $\delta = -2.14$ ppm. The IR spectrum of (TPFC)Ge-H showed an absorption at 2085 cm⁻¹ corresponding to the absorption of Ge-H,¹¹ nearly identical to the Ge-H absorption at 2086 cm⁻¹ for H₂Ge[3,5-(CF₃)₂C₆H₃]₂.^{11*a*} The electronic structure of (TPFC)Ge-H is envisioned as

^a Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China. E-mail: fuxf@pku.edu.cn; Fax: +86 10-6275-1708; Tel: +86 10-6275-6035

^b School of Chemical Sciences, The University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

[†] Electronic supplementary information (ESI) available: The general procedure details of the reactions and spectral data for related complexes. CCDC 839547–839549. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc15076f

[(TPFC)Ge(II)]H where the electron-withdrawing ligand TPFC stabilizes the electron rich metal center.

$$(\text{TPFC})\text{Ge-OCH}_3 \xrightarrow[C_6H_6:CH_3OH=30:1]{} (\text{TPFC})\text{Ge-H}$$
(1)

The unusual α -hydroxyalkyl metal complexes are proposed to be key intermediates in many important catalytic processes¹² which are thermodynamically unstable and prone to dissociation to form a metal hydride complex and an aldehyde.¹³ Reports on the reactivity studies of transition metal hydrides with aldehydes to form α-hydroxyalkyl metal complexes remain limited and representative complexes are rhodium hydride^{4,5} and manganese hydride.¹⁴ Satgé et al. reported that the main group metal hydride R_2GeH_2 (R = phenyl, mesityl) can be deprotonated by tert-butyllithium to form R₂GeHLi which functioned as a strong nucleophile and reacted with benzaldehyde to form the α -hydroxy benzyl germanium complex.^{11b} We observed that in the presence of a catalytic amount of KOH, the reaction of (TPFC)Ge-H with paraformaldehyde at 70 °C in benzene led to the exclusive formation of the α -hydroxy methyl germanium corrole complex (TPFC)Ge-CH₂OH (4) (Scheme 1). Addition of D₂O to the benzene solution of (TPFC)Ge-CH₂OH resulted in the disappearance of the resonance at $\delta = -3.72$ ppm and the doublet at $\delta = -2.20$ ppm collapsed into a singlet, consistent with assignment of the OH and CH₂ protons, respectively. The hemiacetal (TPFC)Ge-CH2OCH2OH was formed through the reaction of (TPFC)Ge-CH2OH with excess formaldehyde when the reaction was performed lower than 70 °C (eqn (2)). The hemiacetal dissociated nearly quantitatively at 70 °C to form (TPFC)Ge-CH₂OH (eqn (2)). The enthalpy and entropy changes for eqn (2) were obtained from variable-temperature ¹H NMR experiments using C₆D₆ as the solvent where ΔH_2 = 57.8 kJ mol⁻¹ and $\Delta S_2 = 1.92 \times 10^2$ J (K·mol)⁻¹. The reaction of (TPFC)Ge-H with benzaldehyde under similar reaction conditions formed the α -hydroxyalkyl product (TPFC)Ge-CH(OH)C₆H₅ (5) (Scheme 1) in 84% yield within 24 hours.

$$(TPFC)Ge-CH_2OH + HCHO
\Rightarrow (TPFC)Ge-CH_2OCH_2OH$$
(2)

The reaction of (TPFC)Ge-H with olefins CH2=CHR $(R = -CO_2CH_3 \text{ and } -CH_2CH_2CH_3)$ was also investigated (Scheme 1). Although no alkyl germanium corrole was observed upon mixing (TPFC)Ge-H with excess of methyl acrylate at 60 °C for 12 hours (Fig. 1a-b), the complex (TPFC)Ge-CH₂CH₂CO₂CH₃ (6) was formed in over 95% yield upon the addition of a catalytic amount of KOH (Fig. 1b-d). Complex 6 was further characterized by molecular structure determination (Fig. 2). A similar result was also observed for the unactivated olefin 1-pentene which formed the corresponding product (TPFC)Ge-CH₂CH₂CH₂CH₂CH₂CH₃ (7) in 50% yield within 24 hours (Scheme 1). The electronwithdrawing ligand TPFC stabilized the carbanion intermediate. The stereo-selectivity is determined by steric hindrance of the ligand where nucleophilic attack occurred at the less crowded terminal olefinic carbon.

There is no reported method for the synthesis of alkyl germanium corrole complexes. Here we demonstrate a simple one-pot synthesis method for preparation of alkyl germanium



Fig. 1 ¹H NMR spectra of (TPFC)Ge-H and (TPFC)Ge-CH₂CH₂CO₂CH₃ at high field. (a) (TPFC)Ge-H; (b) (TPFC)Ge-H plus methyl acrylate at 60 °C for 12 h without addition of KOH. (TPFC)Ge-H plus methyl acrylate at 60 °C with addition of KOH: (c) after 8 h, (d) after 16 h, and (e) after 24 h.



Fig. 2 The structure of 6 illustrated by one of the two independent molecules. Some atom labels are omitted for clarity.

corroles through the reaction of (TPFC)Ge-H with alkyl halides in methanol to form (TPFC)Ge-R (R = CH₃ (8), CH₂C₆H₅ (9)) (Scheme 1). Details of the method are described in ESI.[†] The (TPFC)Ge-R complexes were easily identified by the characteristic ¹H NMR spectra of the alkyl groups. The resonances of axial alkyl hydrogens were shifted to high field positions due to shielding by the ring-current effect of the corrole ligand. Hydrogen atoms on the α -carbon atoms appear at high field ranging from -3.0 to -5.2 ppm (Table S1, ESI[†]) and the phenyl hydrogens of the benzyl group in 9 were split and shifted upfield of their normal diamagnetic positions to 3.60 ppm, 6.16 ppm, and 6.41 ppm. The complex 8 was further characterized by X-ray crystal structure determination and its molecular structure is illustrated in Fig. 3.

The (TPFC)Ge-H is proposed to be rapidly deprotonated in basic solution to form a corrole Ge(II) anion intermediate which subsequently reacts with aldehydes, olefins and alkyl halides to form α -hydroxyalkyl and alkyl germanium products (Scheme 2). When the reaction of (TPFC)Ge-H with methyl acrylate was performed in CD₃OD, the deuterated alkyl germanium product (TPFC)Ge-CH₂CHDCO₂CH₃ was formed while (TPFC)Ge-CH₂CO₂CH₃ was the main product in CD₃OH. These observations indicate that the hydrogen atom on the β -carbon is obtained *via* the protonation of the nucleophilic-addition reaction intermediate by the hydroxyl proton of



Fig. 3 The structure of 8-acetone.



Scheme 2 Reaction pathways of (TPFC)Ge-H with formaldehyde, 1-pentene and methyl iodide.

methanol. Previously, the porphyrin rhodium hydride complex (Por)Rh-H was reported to be deprotonated to form the Rh^I porphyrin anion [(Por)Rh]⁻ which functioned as a nucleophile to react with organic halides, olefins and alkynes to produce metal alkyl complexes.¹⁵

Reactions of late transition metal hydride complexes with unsaturated substrates play a crucial role in many important catalytic processes. We have observed that a main group hydride complex demonstrates parallel reactivity to transition metal hydrides with aldehydes, olefins and alkyl halides to form α -hydroxyalkyl and alkyl complexes. This research demonstrates that the cheaper main-group metal complexes can emulate the reactivity of transition metal complexes although their electronic structures, orbitals and bonding properties are quite different. The main group metal hydrides may function like transition metal hydrides and find wide application in hydrogenations, hydroformylation, and related transformations. Further research focused on the mechanistic study of the substrate reactions of corrole germanium hydrides is under investigation.

We are grateful for support by NSFC Grant 20801002.

Notes and references

- (a) Z. Gross, N. Galili and I. Saltsman, Angew. Chem., Int. Ed., 1999, 38, 1427; (b) Z. Gross, N. Galili, L. Simkhovich, I. Saltsman, M. Botoshansky, D. Bläser, R. Boese and I. Goldberg, Org. Lett., 1999, 1, 599.
- 2 (a) I. Aviv-Harel and Z. Gross, Chem.-Eur. J., 2009, 15, 8382;
 (b) I. Aviv-Harel and Z. Gross, Coord. Chem. Rev., 2011, 255, 717.
- 3 (a) P. J. Brothers, Adv. Organomet. Chem., 2001, 48, 289; (b) P. J. Brothers, Adv. Organomet. Chem., 2000, 46, 223;

(c) M. D. Farnos, B. A. Woods and B. B. Wayland, J. Am. Chem. Soc., 1986, **108**, 3659; (d) J. P. Collman, P. J. Brothers, L. McElwee-White and E. Rose, J. Am. Chem. Soc., 1985, **107**, 6110.

- 4 X. Fu and B. B. Wayland, J. Am. Chem. Soc., 2005, 127, 16460.
- 5 B. B. Wayland, B. A. Woods and V. M. Minda, J. Chem. Soc., Chem. Commun., 1982, 634.
- 6 H. W. Bosch and B. B. Wayland, J. Chem. Soc., Chem. Commun., 1986, 900.
- 7 (a) G. F. Bradley and S. R. Stobart, J. Chem. Soc., Dalton Trans., 1974, 264; (b) R. D. Adams, F. A. Cotton, W. R. Cullen, D. L. Hunter and L. Mihichuk, Inorg. Chem., 1975, 14, 1395; (c) J. A. Connor, P. D. Rose and R. M. Turner, J. Organomet. Chem., 1973, 55, 111; (d) S. Aldridge and A. J. Downs, Chem. Rev., 2001, 101, 3305; (e) A. J. Downs, Coord. Chem. Rev., 1999, 189, 59; (f) E. C. Ashby, J. Organomet. Chem., 1980, 200, 1.
- 8 (a) M. Stender, A. D. Phillips, R. J. Wright and P. P. Power, Angew. Chem., Int. Ed., 2002, 41, 1785; (b) L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead and P. P. Power, J. Am. Chem. Soc., 2003, 125, 11626; (c) G. H. Spikes, Y. Peng, J. C. Fettinger and P. P. Power, Z. Anorg. Allg. Chem., 2006, 632, 1005; (d) R. S. Simons, L. Pu, M. M. Olmstead and P. P. Power, Organometallics, 1997, 16, 1920; (e) X. Wang, Y. Peng, M. M. Olmstead, J. C. Fettinger and P. P. Power, J. Am. Chem. Soc., 2009, 131, 14164; (f) X. Wang, Y. Peng, M. M. Olmstead, H. Hope and P. P. Power, J. Am. Chem. Soc., 2010, 132, 13150; (g) R. S. Simons and P. P. Power, J. Am. Chem. Soc., 1996, 118, 11966; (h) X. Wang, Y. Peng, Z. Zhu, J. C. Fettinger, P. P. Power, J. Guo and S. Nagase, Angew. Chem., Int. Ed., 2010, 49, 4593; (i) G. H. Spikes, J. C. Fettinger and P. P. Power, J. Am. Chem. Soc., 2005, 127, 12232; (j) C. Cui, M. M. Olmstead and P.P. Power, J. Am. Chem. Soc., 2004, 126, 5062; (k) C. Cui, M. Brynda, M. M. Olmstead and P. P. Power, J. Am. Chem. Soc., 2004, 126, 6510; (1) X. Wang, Z. Zhu, Y. Peng, H. Lei, J. C. Fettinger and P. P. Power, J. Am. Chem. Soc., 2009, 131, 6912; (m) Y. Peng, J.-D. Guo, B. D. Ellis, Z. Zhu, J. C. Fettinger, S. Nagase and P. P. Power, J. Am. Chem. Soc., 2009, 131, 16272.
- 9 (a) A. Jana, G. Tavčar, H. W. Roesky and M. John, *Dalton Trans.*, 2010, 9487; (b) A. Jana, D. Ghoshal, H. W. Roesky, I. Objartel, G. Schwab and D. Stalke, *J. Am. Chem. Soc.*, 2009, **131**, 1288; (c) A. Jana, H. W. Roesky and C. Schulzke, *Dalton Trans.*, 2010, 132; (d) A. Jana, S. S. Sen, H. W. Roesky, C. Schulzke, S. Dutta and S. K. Pati, *Angew. Chem., Int. Ed.*, 2009, **48**, 4246.
- (a) S. Nardis, F. Mandoj, R. Paolesse, F. R. Fronczek, K. M. Smith, L. Prodi, M. Montalti and G. Battistini, *Eur. J. Inorg. Chem.*, 2007, 2345; (b) M. Mastroianni, W. Zhu, M. Stefanelli, S. Nardis, F. R. Fronczek, K. M. Smith, Z. Ou, K. M. Kadish and R. Paolesse, *Inorg. Chem.*, 2008, 47, 11680; (c) M. Stefanelli, F. Mandoj, M. Mastroianni, S. Nardis, P. Mohite, F. R. Fronczek, K. M. Smith, K. M. Kadish, X. Xiao, Z. Ou, P. Chen and R. Paolesse, *Inorg. Chem.*, 2011, 50, 8281; (d) L. Simkhovich, A. Mahammed, I. Goldberg and Z. Gross, *Chem.-Eur. J.*, 2001, 7, 1041.
- 11 Typical IR absorption of Ge-H falls in the range of 1953–2175 cm⁻¹. (a) J. E. Bender IV, K. E. Litz, D. Giarikos, N. J. Wells, M. M. Banaszak Holl and J. W. Kampf, *Chem.-Eur. J.*, 1997, **3**, 1793; (b) A. Castel, P. Rivière, J. Satgé and H. Y. Ko, *Organometallics*, 1990, **9**, 205; (c) F. Riedmiller, G. L. Wegner, A. Jockisch and H. Schmidbaur, *Organometallics*, 1999, **18**, 4317; (d) E. J. Kupchik, in *Organotin Compounds*, ed. A. K. Sawyer, Marcel Dekker, New York, vol 1, 1971, pp. 7.
- 12 (a) R. Whyman, A. P. Wright, J. A. Iggo and B. T. Heaton, J. Chem. Soc., Dalton Trans., 2002, 771; (b) D. R. Fahey, J. Am. Chem. Soc., 1981, 103, 136; (c) J. A. Roth and M. Orchin, J. Organomet. Chem., 1978, 172, C27.
- 13 (a) J. A. Gladysz, J. C. Selover and C. E. Strouse, J. Am. Chem. Soc., 1978, 100, 6766; (b) D. L. Johnson and J. A. Gladysz, Inorg. Chem., 1981, 20, 2508.
- 14 (a) G. D. Vaughn, C. E. Strouse and J. A. Gladysz, J. Am. Chem. Soc., 1986, 108, 1462; (b) G. D. Vaughn and J. A. Gladysz, J. Am. Chem. Soc., 1981, 103, 5608.
- 15 H. Ogoshi, J. Setsune, T. Omura and Z. Yoshida, J. Am. Chem. Soc., 1975, 97, 6461.