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Reversible oxidative-addition and reductive-elimination of thiophene from a titanium complex and its thermally-induced hydrodesulphurization chemistry†

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The masked Ti(II) synthon (^{Ket}guan)(η^6-Im^{Dipp}N)Ti (1) oxidatively adds across thiophene to give ring-opened (^{Ket}guan)(Im^{Dipp}N)Ti[κ^2-*S*(CH)$_3$CH] (2). Complex 2 is photosensitive, and upon exposure to light, reductively eliminates thiophene to regenerate 1 – a rare example of early-metal mediated oxidative-addition/reductive-elimination chemistry. DFT calculations indicate strong titanium π-backdonation to the thiophene π^*-orbitals leads to the observed thiophene ring opening across titanium, while a proposed photoinduced LMCT promotes the reverse thiophene elimination from 2. Finally, pressurizing solutions of 2 with H_2 (150 psi) at 80 °C leads to the hydrodesulphurization of thiophene to give the Ti(IV) sulphide (^{Ket}guan)(Im^{Dipp}N)Ti(S) (3) and butane.

The pioneering discovery that Ir^{I}Cl(CO)(PPh$_3$)$_2$ (*i.e.*, Vaska's complex) could intermolecularly cleave chemical bonds, such as H_2 to give Ir^{III}(H)$_2$Cl(CO)(PPh$_3$)$_2$, and then reversibly eliminate the new bonds to fully regenerate the original Ir(I) complex established the underpinnings of transition metal-mediated oxidative-addition (OA)/reductive-elimination (RE) reactions.[1] Since that time, OA/RE reactions have become the cornerstone of many important catalytic cross-coupling transformations.[2] As this chemical phenomenon requires two-electron redox cycling at the metal centre, precious metal catalysts have proven effective in OA/RE reactions.[3] However, the sustainability of precious metals and their inherent toxicity have prompted quests for viable alternatives.[4]

In this regard, much attention has been devoted to the development of late 3d-metal OA/RE catalysts;[5] yet, the abundance of early-metals (groups 3–5) and their relatively low toxicity offer viable alternatives. While it is well-established that low valent early-metals (electron counts $\geq d^2$) can undergo two-electron OA reactions, including across C–H bonds,[6] the reverse RE is more challenging.[7] At issue, in these highly electropositive metals, is their thermodynamic preference for higher oxidation states, which provides a significant barrier for reversible two-electron chemistry.[8,9]

Heyduk and Wolczanski have circumvented the limited redox chemistry of early-metals by employing redox non-innocent ligands with formally d^0 metal centres in the complexes [NNN^{cat}]Zr=NAr(Cl)(CN^{t}Bu) (NNN^{cat}=(2-^{i}PrN-4-OMe-C$_6$H$_3$)$_2$N)[10] and (dadi)Ti=NAd (dadi = [{–CH=N(1,2-C$_6$H$_4$)N(2,6-^{i}Pr$_2$-C$_6$H$_3$)}$_2$]),[11] respectively, to perform nitrene transfer reactions. In these cases, the metal acts as a redox conduit, transferring electrons to and from the noninnocent ligand while facilitating substrate reactivity and bond formations.[12]

Nonetheless, substrate-induced RE reactions involving early-metals is precedented whereby an added reagent initiates reductive ligand displacement or reacts with coordinated molecules to generate a low-valent metal species.[13] Tonks *et al.* have elegantly capitalized on this phenomenon for the multi-component, titanium-catalyzed [2+2+1] reaction for the synthesis of tetrasubstituted pyrroles.[14] The proposed mechanism involves the sequential addition of two alkyne equivalents across a Ti(IV) imido to generate an azatitanacyclohexadiene complex, which reductively eliminates the N-heterocycle to generate a proposed masked Ti(II) species that subsequently reacts with diazene to reform the catalytically active Ti(IV) starting complex.[15]

It still remains the case that examples of non-substrate-induced early-metal OA/RE are extremely limited. In principle, group 3–5 complexes that exhibit reversible OA/RE chemistry, especially those involving C–X bonds, can provide critical insights for the development of new early-metal redox catalysts.

In our laboratory, we have been exploring the chemistry of the masked titanium complex (^{Ket}guan)(η^6-Im^{Dipp}N)Ti (**1**) (Scheme 1), which behaves as a Ti(II) synthon.[6a,16] Complex **1** is unique as we have shown that it exhibits precious metal type reactivity in the catalytic transfer hydrogenation of cyclic olefins.[6a] Based upon this, we have begun to further explore the extent of late metal mimicry in **1**, especially its ability to participate in two-electron redox cycling. Herein, we show that **1** undergoes OA of thiophene to give the ring-opened thiotitanocycle complex (^{Ket}guan)(Im^{Dipp}N)Ti[κ^2-*S*(CH)$_3$*C*H] (**2**). Complex **2** is stable in solution to at least 80 °C, but upon

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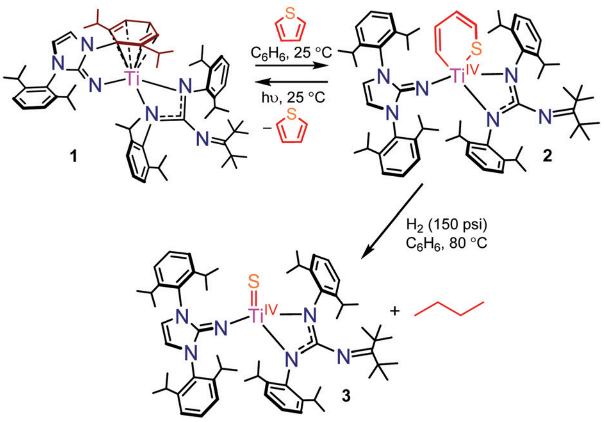

Scheme 1 Synthesis, photochemistry, and HDS reactivity of **2**.

exposure to ambient light regenerates **1** and free thiophene – demonstrating a fully reversible OA/RE process mediated by titanium. Insights into the ring opening mechanism are provided through computational analysis. Finally, we show that heating solutions of **2** in the presence of H_2 promotes the hydrodesulphurization (HDS) of the thiophene to give the previously reported Ti(IV) sulphide (^{Ket}guan)(Im^{Dipp}N)Ti(S) (**3**) and butane (Scheme 1).[16]

Treatment of a dark-brown solution of **1** in C_6D_6 with one equiv of thiophene gives an orange solution with quantitative formation of a new diamagnetic product as observed by ^1H NMR spectroscopy. In addition to the characteristic peaks of the supporting ligands, new resonances appearing from 6.25 to 7.31 ppm are observed (Fig. S1, ESI†), assignable to the H_α–H_δ protons of a thiophene derived moiety, signalling the formation of **2** (Scheme 1). In line with this, the chemical shifts of these peaks are similar to the range reported for the proton resonances of ring-opened thiophene in $Cp_2W[\kappa^2\text{-}S(CH)_3CH]$.[17]

Single crystals of $\mathbf{2}\cdot1.5C_6H_{14}$ are grown from the storage of a concentrated hexanes/toluene solution at −32 °C for two days. The solid-state molecular structure of $\mathbf{2}\cdot1.5C_6H_{14}$ is presented in Fig. 1 and clearly shows the insertion of titanium into the C–S bond of thiophene to give a six-membered titanocycle. The Ti1–S1 = 2.4052(9) Å and Ti1–C1 = 2.040(3) Å bond distances and C1–Ti1–S1 = 86.8(1)° bond angle are unremarkable, while the C1–C2 = 1.297(5) Å, C2–C3 = 1.459(5) Å, C3–C4 = 1.348(5) Å and S1–C4 = 1.721(3) Å distances of the ring are consistent with localized 1,3-butadiene character, similar to that of $Cp_2W[\kappa^2\text{-}S(CH)_3CH]$.[17]

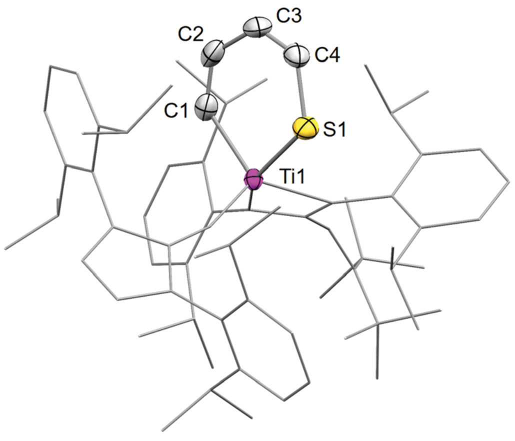

Fig. 1 Solid-state molecular structure of $\mathbf{2}\cdot1.5C_6H_{14}$ with the atoms of the co-crystallized solvent molecules omitted for clarity.

Notably, **2** represents the first example of an early-metal thiometallacycle formed from the OA of the metal across the thiophene C–S bond.[18] Moreover, the formation of **2** under mild conditions differs from the synthesis of nearest-neighbour group 6 ring-opened thiophene derivatives which typically require photolysis or heating to promote thiophene activation,[17,19] with the exception of $Mo(PMe_3)_6$ which reacts with thiophene at room temperature to give $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$.[20]

Importantly, in our case, the OA of thiophene to **1** is thermodynamically favoured (*vide infra*), while the RE of pyrrole is preferred in Tonks' titanium-catalysed reactions.[14,15] This is surprising as the azaphilicity of titanium leads to strong Ti–N bonding; however, the difference in these two systems may be a consequence of relative aromaticity values that favour the formation of pyrrole. Yet, this is an oversimplification and warrants further study. Regardless, the RE of thiophene from **2** can be induced under mild conditions. Photolyzing aromatic solutions of **2** with blue LED light leads to the formation of **1** and thiophene as shown by monitoring the reactions by ^1H NMR and UV-vis spectroscopies (Fig. S6 and S9, ESI†). The complete reversion is only possible in dilute solutions (*ca.* 5 mM) as **1** immediately back reacts with thiophene to regenerate **2**, especially in the absence of light.

This data clearly points to a fully reversible OA/RE mechanism at titanium which interconverts **1** and **2** under mild conditions. It must be said that photolysis of $Cp_2Ti(\kappa^2\text{-}SC_6H_4\text{-}2\text{-}Ph)$ solutions in the presence of CO does reductively eliminate dibenzothiophene (DBT) to give $Cp_2Ti(CO)_2$, which is unreactive to the free DBT.[2b] Moreover, this reversible OA/RE behaviour is not documented among group 6 ring-opened thiophene derivative complexes, some of which have been called reductively inert.[19a] While the C–S bond cleavage of thiophene by precious metals has been extensively studied,[21] it seems only one example of reversible OA/RE of thiophene has been documented where $Pt(PEt_3)_3$ reversibly ring-opens thiophenes in solution between 80–100 °C when in the presence of excess PEt_3.[21,22]

Utilizing a truncated model where the isopropyl groups of **1** have been replaced for ethyl groups ($\mathbf{1^{Et}}$) (see Fig. 2 and ESI† for computational details), DFT calculations reveal the initial coordination of thiophene to the unmasked titanium is unlikely to proceed *via* η^1-sulphur binding as this leads to a relatively higher energy intermediate (**B**, 21.2 kcal mol^{-1}) (Fig. 2). Additionally, attempts to find η^2-bound isomers, *e.g.* along C2–C3, were unsuccessful and implies that these structures are not local minima of the potential energy surface. This differs from the calculated mechanisms of the late-metal complexes [Pt(dmpe)] and $[(C_5Me_5)Rh(PMe_3)]$ in their interactions with thiophene that show a variety of initial η^2- and η^3-binding modes,[23] suggesting the structural diversity that represents the early stage of thiophene activation by these late transition metals is absent in our titanium system.

Instead, coordination to the titanium appears to initially take place through the π-system of thiophene in an η^3-fashion

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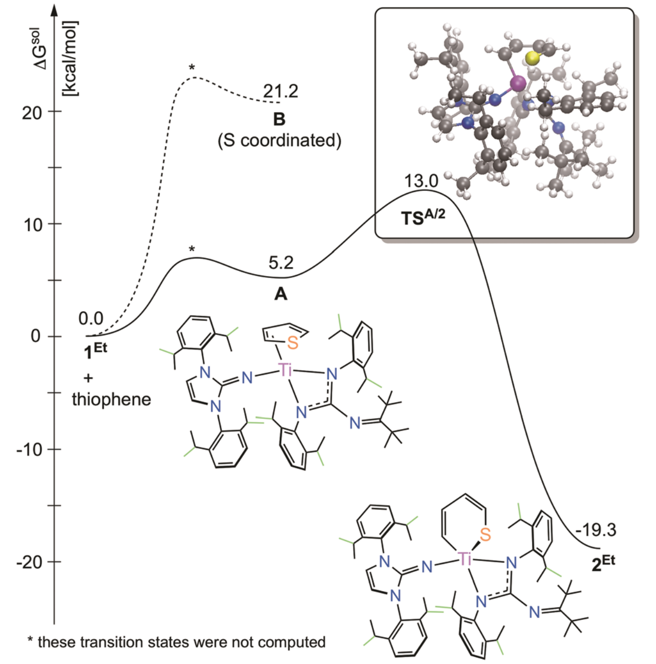

Fig. 2 Solution-state Gibbs free energy profile of $\mathbf{1}^{\mathbf{Et}}$ + thiophene → $\mathbf{2}^{\mathbf{Et}}$, given together with the structure of $\mathbf{TS}^{\mathbf{A/2}}$. Drawings show the truncation (highlighted in green) applied to the *in silico* models.

along the S1–C1–C2 fragment, leading to intermediate **A** with a relative stability of 5.2 kcal mol^{-1} (Fig. 2). Subsequently, the breaking of the S1–C1 bond takes place through an elementary step traversing $\mathbf{TS}^{\mathbf{A/2}}$ with a relative solution state Gibbs free energy of 13 kcal mol^{-1}, leading directly to the Ti(IV) product $\mathbf{2}^{\mathbf{Et}}$. The reaction is computed to be exergonic by 19 kcal mol^{-1}, which is reasonable given the intrinsic thermodynamic instability of Ti(II) centers.

The HOMO of **A** (Fig. S12, ESI†) clearly shows π-back-donation from the Ti(II) center to one of the π*-orbitals of thiophene, leading to the η^3-type binding at the S1–C1–C2 moiety. Going from **A** to $\mathbf{TS}^{\mathbf{A/2}}$, the torsion of the thiophene moiety transforms this π*-orbital into an antibonding σ*-orbital between S1–C1, a directly recognizable feature of the HOMO of $\mathbf{TS}^{\mathbf{A/2}}$ (Fig. S12, ESI†). Consequently, the increased relative contribution of the thiophene-centred atomic orbitals results in metal-to-ligand charge transfer, a hallmark of OA, leading to the complete cleavage of the S1-C1 bond and formation of **2**. Accordingly, the HOMO−4 of $\mathbf{2}^{\mathbf{Et}}$ (Fig. S12, ESI†) is one of the MOs representing the Ti-thiophene σ-interactions, and its features signal a completed OA with formal $SC_4H_4{}^{2-}$ and Ti(IV) fragments.

TD-DFT simulations were also carried out to illuminate the electronic transitions of $\mathbf{2}^{\mathbf{Et}}$ that would plausibly induce thiophene elimination. The electronic absorptions of $\mathbf{2}^{\mathbf{Et}}$ are calculated at 440, 402, 396, and 370 nm, which corroborate nicely with the absorption features of **2** at 445, 390, and 345 nm (Fig. S9, ESI†). The calculated absorptions at 440 and 396 nm may be formally described as HOMO → LUMO+1 and HOMO → LUMO+2 transitions (Fig. S13, ESI†), respectively, corresponding to ring-opened thiophene π-orbital (HOMO) to empty metal d-orbitals (LUMO+1, LUMO+2) excitation.[24] While the exact mechanism is not clear, we posit the excitation process leads to sufficient ligand-to-metal charge transfer such as to oxidize the thiometallacycle fragment and consequently reduce the titanium centre, thus initiating the cascade of electronic structural changes leading to thiophene RE from **2**. Importantly, this differs from the typical substrate-induced RE chemistry of early-metal systems, where the incoming substrate effectively acts as a two-electron oxidant to promote product release.[25]

To support our assessments, photochemical experiments were carried out using a broadband light source with a cutoff filter to exclude higher energy wavelengths (<400 nm). Under this exclusion, photolysis of **2** did not lead to any observed reaction, thus eliminating the 445 nm absorption as a pertinent transition. However, photolyzing solutions of **2** within the wavelength range of 385–430 nm promotes RE of thiophene, lending credence to the calculated LMCT assignment at 396 nm.

It was noted in the reactivity study of $Pt(PEt_3)_3$ with thiophenes, that the reversible OA/RE mechanism has important implications as it pertains to understanding the catalytic HDS process of thiophenes and designing new catalysts.[22] To this end, we have been exploring the viability of utilizing **2** to effect the HDS of thiophene, an industrially relevant transformation.[19d,26]

Pressurizing solutions of **2** (*ca.* 0.02 mM) in C_6D_6 with H_2 (150 psi) under the strict exclusion of light fails to produce any reactivity after one day at room temperature. Yet, heating this mixture to 80 °C for several days leads to the formation of the previously reported titanium sulphide **3** in 52% yield (Scheme 1).[16] Butadiene or butene are common HDS products in homogeneous systems;[26b] however, no resonances matching these organics were observed in the ^1H NMR spectrum. Instead, a series of multiplets appears at 0.87 and 1.24 ppm (Fig. S7, ESI†), corresponding to the proton signals of *n*-butane as confirmed by comparison against an external standard (Fig. S8, ESI†).

The formation of butane in this reaction is surprising as it suggests a multi-step mechanism involving hydrogenation and hydrogenolysis reactions.[26a] NMR spectroscopic analysis of the reaction mixture does not show any resonances attributable to intermediates. Nonetheless, this reactivity is in-line with a few precious metal systems which have been shown capable of HDS to give butane. For instance, Vicic and Jones have reported the HDS of thiophene by $Cp^*Ir(H)(Cl)[\kappa^2\text{-}S(CH)_3CH]$ in the presence of H_2.[26a] The reaction produces an isolable bimetallic, bridging thiolate that can be further reacted with H_2 to eliminate butane and form unknown iridium products. In our case, the reaction leads to the formation of a stable terminal sulphide complex.

In the study of nickel-based, homogenous thiophene HDS, Jones and co-workers invoked the formation of a rare terminal nickel sulphide, *viz.* $[(^iPr_2P)_2CH_2CH_2]Ni{=}S$, as a critical intermediate in their reaction, while stressing the importance of terminal metal-sulphides as possible transients/intermediates in both homogeneous and heterogeneous HDS processes.[27] Notably, the formation of **3** represents the first isolable example of a terminal metal-sulphide isolated from a thiophene HDS reaction. It is known that Ti═S bonds can be sensitive to H_2 activation,[28] and while we have not yet observed any reductive loss of the sulphide ligand from **3** under the conditions of our experiments, we are investigating the potential of **1** to effect HDS catalysis of thiophenes under higher pressures. We are also studying the reactivity of **1** towards ring expanded thiophenes, *e.g.* benzothiophene, and other heteroatom donors.

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In conclusion, we have shown the masked Ti(II) synthon, **1**, is capable of effecting the reductive ring-opening of thiophene to give the thiotitanocycle complex **2**. This OA of thiophene is the first for an early-metal complex, and DFT calculations suggest the ring-opening mechanism initiates *via* η^3-coordination of thiophene to an unmasked Ti(II) centre and subsequent back-donation into the thiophene π^*-orbitals. Remarkably, **2** is photosensitive and reductively eliminates thiophene to regenerate **1**. This process is an exceedingly rare example of a fully reversible, non-substrate induced OA/RE mechanism mediated by an early-metal. Capitalizing on the activation of thiophene, pressurizing solutions of **1** with H_2 (150 psi) at 80 °C leads to HDS concomitant with the formation of butane. These results show that base metals, such as titanium, have the potential to act as precious metal surrogates. As the reversible redox cycling of Vaska's complex provided the foundation for modern precious metal catalysis, our system may provide a unique platform for the development of new early-metal redox catalysts – a major advantage given the abundance and low-toxicity of titanium. Yet, much remains to be learned on how to best access and optimize the ligand environments and electronic structure of the early metal complexes to harness such reactivity. In this regard, our studies of **1** are ongoing.

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Conflicts of interest

The authors declare no competing financial interests.

Notes and references

1 (*a*) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, 1962, **84**, 679–680; (*b*) D. A. Wink and P. C. Ford, *J. Am. Chem. Soc.*, 1985, **107**, 5566–5567.

2 (*a*) F. Diederich, *Metal catalyzed cross coupling reactions*, Wiley-VCH, Weinheim, 2001; (*b*) P. R. Stafford, T. B. Rauchfuss, A. K. Verma and S. R. Wilson, *J. Organomet. Chem.*, 1996, **526**, 203–214.

3 J. A. Labinger, *Organometallics*, 2015, **34**, 4784–4795.

4 J. R. Ludwig and C. S. Schindler, *Chem*, 2017, **2**, 313–316.

5 (*a*) R. Arevalo and P. J. Chirik, *J. Am. Chem. Soc.*, 2019, **141**, 9106–9123; (*b*) A. Fürstner, *ACS Cent. Sci.*, 2016, **2**, 778–789; (*c*) A. Piontek, E. Bisz and M. Szostak, *Angew. Chem., Int. Ed.*, 2018, **57**, 11116–11128; (*d*) T. Zell and R. Langer, *ChemCatChem*, 2018, **10**, 1930–1940; (*e*) P. L. Holland, *Acc. Chem. Res.*, 2015, **48**, 1696–1702.

6 (*a*) J. R. Aguilar-Calderon, A. J. Metta-Magana, B. Noll and S. Fortier, *Angew. Chem., Int. Ed.*, 2016, **55**, 14101–14105; (*b*) B. D. Steffey, L. R. Chamberlain, R. W. Chesnut, D. E. Chebi, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1989, **8**, 1419–1423; (*c*) J. S. Yu, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1990, **112**, 8171–8172; (*d*) J. S. Figueroa, N. A. Piro, D. J. Mindiola, M. G. Fickes and C. C. Cummins, *Organometallics*, 2010, **29**, 5215–5229; (*e*) M. Tayebani, K. Feghali, S. Gambarotta and G. Yap, *Organometallics*, 1998, **17**, 4282–4290; (*f*) P. N. Riley, J. R. Clark, P. E. Fanwick and I. P. Rothwell, *Inorg. Chim. Acta*, 1999, **288**, 35–39.

7 H. Kawaguchi and T. Matsuo, *J. Am. Chem. Soc.*, 2003, **125**, 14254–14255.

8 J. D. Guo, X. Deng, C. Y. Song, Y. Lu, S. L. Qu, Y. F. Dang and Z. X. Wang, *Chem. Sci.*, 2017, **8**, 2413–2425.

9 Of note, $Cp^*{}_2Ti$ is observed to undergo reversible intramolecular C-H addition, tautomerizing between $Cp^*{}_2Ti^{II}$ and $Cp^*(\eta^6\text{-}C_5Me_4CH_2)Ti^{IV}\text{-}H$ in solution, though pathways other than RE can be invoked to explain the reformation of $Cp^*{}_2Ti^{II}$. See ref. 29.

10 A. I. Nguyen, R. A. Zarkesh, D. C. Lacy, M. K. Thorson and A. F. Heyduk, *Chem. Sci.*, 2011, **2**, 166–169.

11 S. P. Heins, P. T. Wolczanski, T. R. Cundari and S. N. MacMillan, *Chem. Sci.*, 2017, **8**, 3410–3418.

12 R. F. Munha, R. A. Zarkesh and A. F. Heyduk, *Dalton Trans.*, 2013, **42**, 3751–3766.

13 (*a*) K. I. Gell and J. Schwartz, *J. Am. Chem. Soc.*, 1981, **103**, 2687–2695; (*b*) H.-C. Chiu and I. A. Tonks, *Angew. Chem., Int. Ed.*, 2018, **57**, 6090–6094; (*c*) E. P. Beaumier, M. E. McGreal, A. R. Pancoast, R. H. Wilson, J. T. Moore, B. J. Graziano, J. D. Goodpaster and I. A. Tonks, *ACS Catal.*, 2019, **9**, 11753–11762.

14 A. J. Pearce, X. Y. See and I. A. Tonks, *Chem. Commun.*, 2018, **54**, 6891–6894.

15 Z. W. Davis-Gilbert, X. Wen, J. D. Goodpaster and I. A. Tonks, *J. Am. Chem. Soc.*, 2018, **140**, 7267–7281.

16 J. R. Aguilar-Calderon, J. Murillo, A. Gomez-Torres, C. Saucedo, A. Jordan, A. Metta-Magana, M. Pink and S. Fortier, *Organometallics*, 2019, DOI: 10.1021/acs.organomet.9b00637.

17 W. D. Jones, R. M. Chin, T. W. Crane and D. M. Baruch, *Organometallics*, 1994, **13**, 4448–4452.

18 The related titanium and zirconium ring-opened thiophene derivatives $Cp_2Ti(\kappa^2\text{-}SC_6H_4\text{-}2\text{-}Ph)_4$ and $Cp_2Zr[\kappa^2\text{-}S(CH)_3C(SiMe_3)]$ are known, with the former synthesized through salt metathesis using a lithium arylsulphide and the latter formed through migratory ring enlargement and dyotropic rearrangement. See ref. 30.

19 (*a*) D. G. Churchill, B. M. Bridgewater and G. Parkin, *J. Am. Chem. Soc.*, 2000, **122**, 178–179; (*b*) A. Sattler, K. E. Janak and G. Parkin, *Inorg. Chim. Acta*, 2011, **369**, 197–202; (*c*) A. Sattler and G. Parkin, *J. Am. Chem. Soc.*, 2011, **133**, 3748–3751; (*d*) D. Buccella, K. E. Janak and G. Parkin, *J. Am. Chem. Soc.*, 2008, **130**, 16187–16189; (*e*) R. C. Mills, K. A. Abboud and J. M. Boncella, *Chem. Commun.*, 2001, 1506–1507.

20 K. E. Janak, J. M. Tanski, D. G. Churchill and G. Parkin, *J. Am. Chem. Soc.*, 2002, **124**, 4182–4183.

21 R. J. Angelici, *Organometallics*, 2001, **20**, 1259–1275.

22 J. J. Garcia, B. E. Mann, H. Adams, N. A. Bailey and P. M. Maitlis, *J. Am. Chem. Soc.*, 1995, **117**, 2179–2186.

23 (*a*) T. A. Atesin and W. D. Jones, *Inorg. Chem.*, 2008, **47**, 10889–10894; (*b*) T. A. Atesin and W. D. Jones, *Organometallics*, 2008, **27**, 3666–3670; (*c*) T. A. Atesin and W. D. Jones, *Organometallics*, 2008, **27**, 53–60.

24 The HOMO−1 of **2** is a guanidinate NCN-based π-orbital, and the corresponding excitations at 402 and 370 nm to LUMO+1 and LUMO+2 are inconsequential to the observed thiophene RE chemistry.

25 J. D. Guo, Y. Lu, R. H. Zhao, Z. Y. Liu, W. Menberu and Z. X. Wang, *Chem. – Eur. J.*, 2018, **24**, 7010–7025.

26 (*a*) D. A. Vicic and W. D. Jones, *Organometallics*, 1997, **16**, 1912–1919; (*b*) C. Bianchini and A. Meli, *Acc. Chem. Res.*, 1998, **31**, 109–116.

27 D. A. Vicic and W. D. Jones, *J. Am. Chem. Soc.*, 1999, **121**, 7606–7617.

28 Z. K. Sweeney, J. L. Polse, R. G. Bergman and R. A. Andersen, *Organometallics*, 1999, **18**, 5502–5510.

29 (*a*) J. Pinkas, R. Gyepes, I. Cisarova, J. Kubista, M. Horacek and K. Mach, *Dalton Trans.*, 2017, **46**, 8229; (*b*) J. E. Bercaw, *J. Am. Chem. Soc.*, 1974, **96**, 5087.

30 (*a*) P. R. Stafford, T. B. Rauchfuss, A. K. Verma and S. R. Wilson, *J. Organomet. Chem.*, 1996, **526**, 203; (*b*) G. Erker, R. Petrenz, C. Krueger, F. Lutz, A. Weiss and S. Werner, *Organometallics*, 1992, **11**, 1646.

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