Selective Catalytic Dimerisation of Ethylene to But-1-ene by $[(\eta\text{-}C_5Me_5)Ta(PMe_3)(H)(Br)(\eta^2\text{-}CHPMe_2)]$

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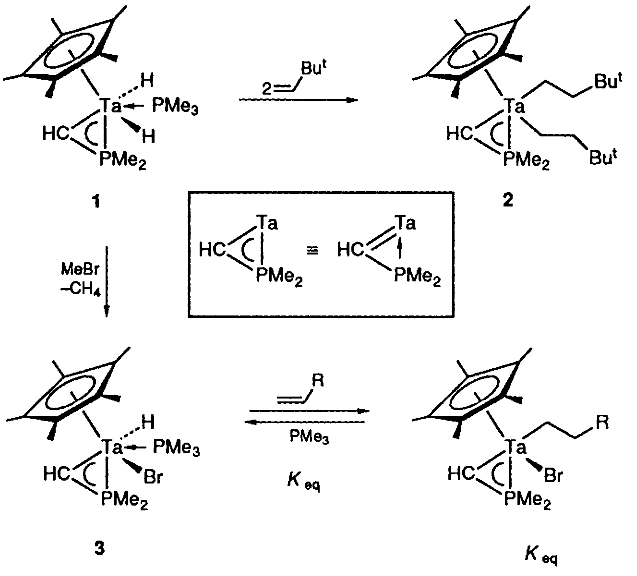
$[(\eta\text{-}C_5Me_5)Ta(PMe_3)(H)(Br)(\eta^2\text{-}CHPMe_2)]$ reacts with an excess of ethylene at 70 °C to give but-1-ene cleanly and selectively.

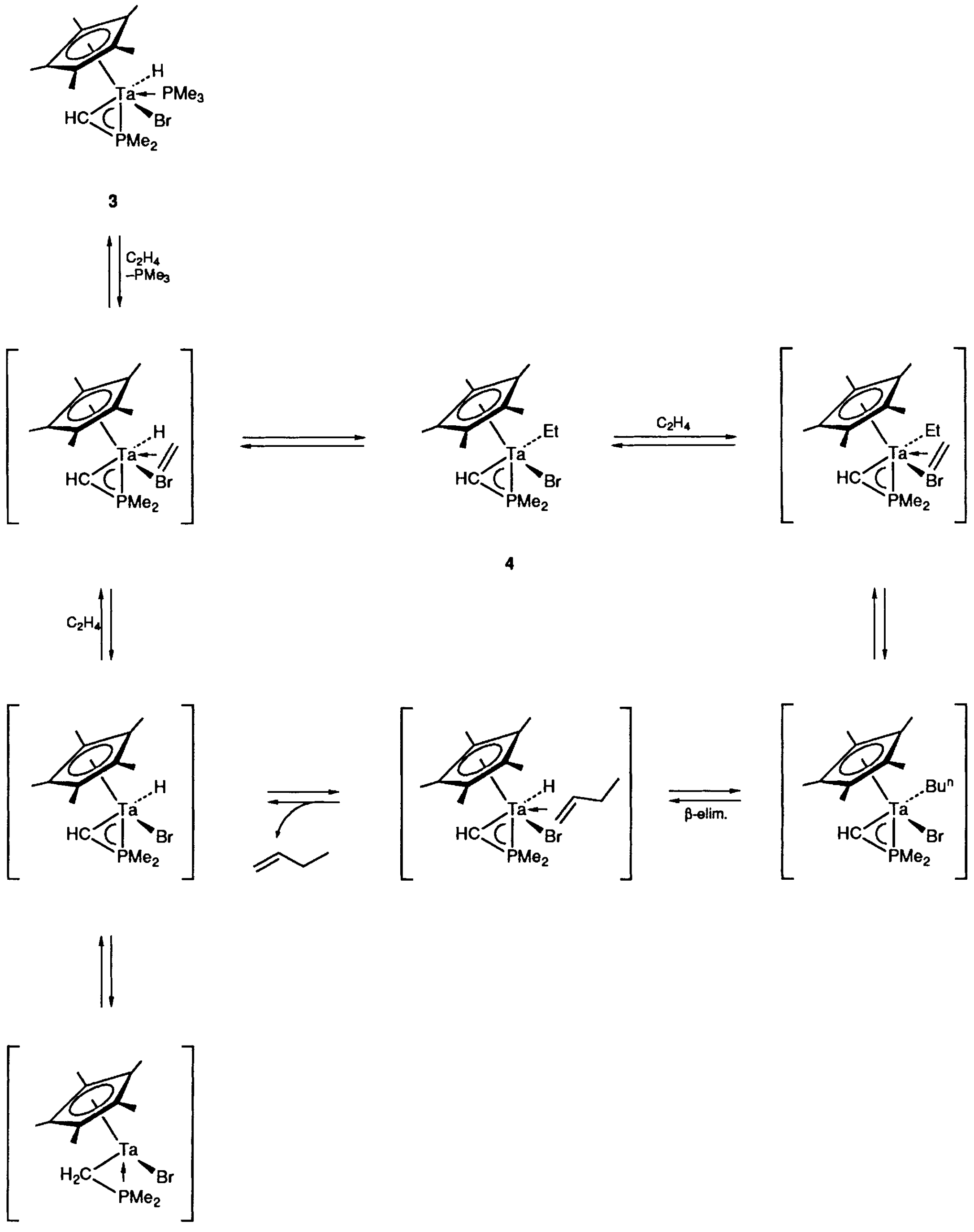
Coordinatively unsaturated transition metal hydride and alkyl complexes are important intermediates in the catalytic dimerisation, oligomerisation and polymerisation of alkenes.[1] Although these species are traditionally generated *in situ* through treatment of an appropriate transition metal halide with a Lewis acid co-catalyst, there has been growing interest in the development of single component, Lewis acid-free catalysts, particularly for alkene polymerisation.[2] In general, it is found that high-oxidation-state, fourteen-electron alkyl complexes of the early transition metals are particularly appropriate for alkene oligomerisation and polymerisation *via* a direct insertion (Cossee–Arlman-type) mechanism.[3] Multiple alkene insertions generally occur less readily for sixteen-electron alkyl complexes and these, therefore, offer more potential for dimerisation and oligomerisation processes.

Recently, we showed that t-butylethylene inserts into the Ta–H bonds of $[(\eta\text{-}C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)]$ **1** to give the sixteen-electron dialkyl $[(\eta\text{-}C_5Me_5)Ta(CH_2CH_2Bu^t)_2(\eta^2\text{-}CHPMe_2)]$[4] **2** (Scheme 1). We also noted that the reaction of **1** with ethylene is more complex, affording a mixture of unidentified tantalum alkyls and free alkenes; this reaction is still under investigation.

Here, we show that by exchanging one of the hydrides of **1** for a halide ligand, its reactivity towards ethylene may be moderated to allow a clean and selective dimerisation of ethylene to but-1-ene. Only after all the excess of ethylene has been consumed is isomerisation of but-1-ene to the internal alkene observed. The mono-bromide derivative **3** is accessible *via* the reaction of **1** with a molar equivalent of MeBr.[5] Complex **3** reacts rapidly with ethylene and mono-substituted alkenes, $CH_2{=}CHR$ (R = Me, Bu^t or Ph), at room temperature to establish an equilibrium with the alkyl derivatives $[(\eta\text{-}C_5Me_5)Ta(Br)(CH_2CH_2R)(\eta^2\text{-}CHPMe_2)]$ (R = H **4**, Me **5**, Bu^t **6**, or Ph **7**) which have been characterized by ^{1}H NMR



R =		K_{eq}
H	4	8.7(2)
Me	5	$3.5(2) \times 10^{-2}$
Bu^t	6	$1.1(1) \times 10^{-1}$
Ph	7	$5.2(2) \times 10^{-3}$



spectroscopy only.† Complexes **4**–**7** are unstable in the absence of an excess of alkene owing to the propensity for β-elimination and loss of alkene. However, warming an equilibrium mixture of **3** and **4** at 70 °C in the presence of an excess of ethylene results in a clean and selective dimerisation of ethylene to but-1-ene (by ^{1}H NMR). The reaction is catalytic in **4**, although fairly slow under these conditions, giving *ca.* 5.5 turnovers in 3.5 h for a 20-fold excess of ethylene. A possible catalytic cycle for this reaction is shown in Scheme 2.

Neither the intermediate n-butyl-Ta species nor the metal–alkene adducts are observable (by ^{1}H NMR) under these conditions; they are presumed to be either too unstable or too labile. The mechanism shown in Scheme 2 involves direct insertion of ethylene into the Ta–C bond, although, at this stage, an alternative pathway involving metallacycles[6] cannot be ruled out since the reaction of **3** with C_2D_4 results in deuterium incorporation into the metallacycle methine

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† Selected ^{1}H NMR data (C_6D_6, 250 MHz, 298 K) for **4**: δ 9.59 (s, 1H, C*H*PMe$_2$), 1.83 (s, 15H, C_5Me_5), 1.72 (d, 3H, $^{2}J_{PH}$ 10.4 Hz, P*Me*$_2$), 1.53 (d, 3H, $^{2}J_{PH}$ 9.8 Hz, P*Me*$_2$), 1.22 (t, 3H, $^{3}J_{HH}$ 8.0 Hz, CH_2CH_3), and 0.70 (m, 2H, CH_2CH_3). For **5**: δ 9.65 (s, 1H, C*H*PMe$_2$), 1.83 (s, 15H, C_5Me_5), 1.71 (d, 3H, $^{2}J_{PH}$ 10.8 Hz, P*Me*$_2$), and 1.18 (t, 3H, $^{3}J_{HH}$ 8.0 Hz, $CH_2CH_2CH_3$), methylene signals not resolved. For **6**: δ 9.63 (s, 1H, C*H*PMe$_2$), 1.85 (s, 15H, C_5Me_5), 1.71 (d, 3H, $^{2}J_{PH}$ 10.3 Hz, P*Me*$_2$), 1.59 (d, 3H, $^{2}J_{PH}$ 9.7 Hz, P*Me*$_2$), and 0.10 (s, 9H, $CH_2CH_2CMe_3$), methylene signals not resolved. For **7**: δ 9.74 (s, 1H, C*H*PMe$_2$), 1.81 (s, 15H, C_5Me_5), 1.71 (d, 3H, $^{2}J_{PH}$ 10.6 Hz, P*Me*$_2$), and 1.63 (d, 3H, $^{2}J_{PH}$ 11.1 Hz, P*Me*$_2$).

hydrogen site, implying an equilibrium with a $Ta(CH_2PMe_2)$ species and thus allowing for the possibility of an alkene coupling pathway[6] *via* $[(\eta\text{-}C_5Me_5)Ta(CH_2PMe_2)(Br)]$. However, no metallacycle intermediates are observable by ^1H NMR. New alkene resonances attributable to but-2-ene are eventually observed but only after all the ethylene has been consumed; this may suggest that but-1-ene either does not compete effectively with ethylene for the vacant coordination site of the base-free hydrido-bromide and/or that the insertion of but-1-ene into the Ta–H bond to give a secondary Ta alkyl is disfavoured. Support for the above is found by comparing the K_{eq} values for alkene insertion given in Scheme 1 where it is seen that insertion of monosubstituted alkenes is significantly less favourable than for ethylene. Furthermore, insertion is highly regioselective, in all cases forming the primary alkyl product exclusively. Although the rate of ethylene dimerisation is slow, this is a model system which is quite remarkable in its selectivity.

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References

1 For leading references, see W. Keim, A. Behr and M. Roper in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, vol. 8, ch. 52.

2 G. G. Hlatky, H. W. Turner and R. R. Eckman, *J. Am. Chem. Soc.*, 1989, **111**, 2728; R. F. Jordan, R. E. Lapointe, C. S. Bajgur, S. F. Echols and R. Willet, *J. Am. Chem. Soc.*, 1987, **109**, 4111; B. J. Burger, M. E. Thompson, D. W. Cotter and J. E. Bercaw, *J. Am. Chem. Soc.*, 1990, **112**, 1566; M. Brookhart, A. F. Volpe, Jr., D. M. Lincoln, I. T. Horváth and J. M. Millar, *J. Am. Chem. Soc.*, 1990, **112**, 5634; R. Taube and L. Krukowka, *J. Organomet. Chem.*, 1988, **347**, C9; R. F. Jordan, C. S. Bajgur, R. Willet and B. Scott, *J. Am. Chem. Soc.*, 1986, **108**, 7410; P. J. Shapiro, E. Brunel, W. P. Schaefer and J. E. Bercaw, *Organometallics*, 1990, **9**, 867; R. F. Jordan, *J. Chem. Educ.*, 1988, **65**, 285.

3 E. J. Arlman and P. Cossee, *J. Catal.*, 1964, **3**, 99.

4 V. C. Gibson, T. P. Kee and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1990, 313.

5 T. P. Kee, V. C. Gibson and W. Clegg, *J. Organomet. Chem.*, 1987, **325**, C14; H. M. Anstice, H. H. Fielding, V. C. Gibson, C. E. Housecroft and T. P. Kee, manuscript in preparation.

6 J. D. Fellmann, G. A. Rupprecht and R. R. Schrock, *J. Am. Chem. Soc.*, 1979, **101**, 5099; S. Datta, M. B. Fisher and S. S. Wreford, *J. Organomet. Chem.*, 1980, **188**, 353; R. R. Schrock, S. McLain and J. Sancho, *Pure Appl. Chem.*, 1980, **52**, 729.