Facile C–H Activation by Lutetium–Methyl and Lutetium–Hydride Complexes

Patricia L. Watson

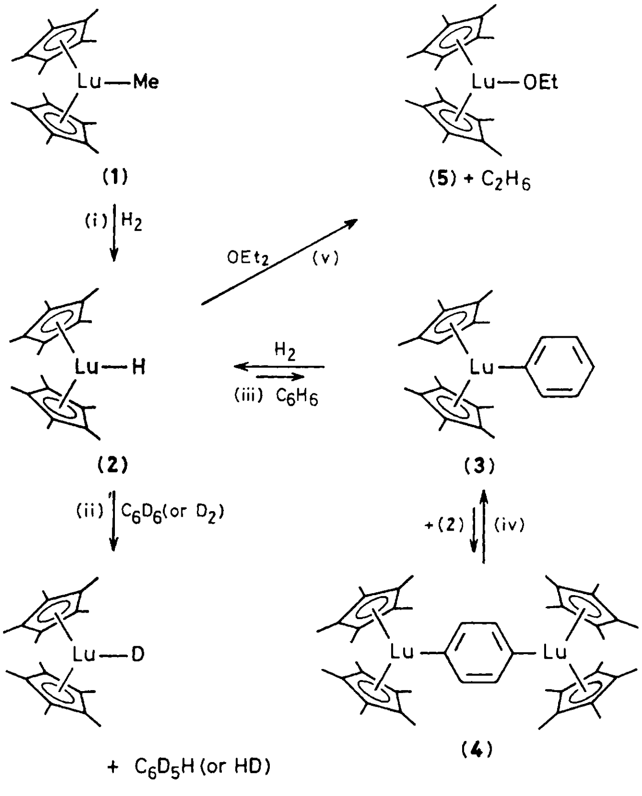
Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware, 19898, U.S.A.

Bis(pentamethylcyclopentadienyl)lutetium complexes Lu(η^5-C_5Me_5)$_2$R (R = Me, H) react at 20—50 °C in hydrocarbon solvents with benzene, pyridine, the ylide CH_2PPh_3, and tetramethylsilane to give stable, isolatable products of C–H activation, *i.e.* metallation at a carbon of the reagent with extrusion of R–H.

I report here that lutetium–alkyl and –hydride derivatives can activate sp^2 C–H bonds in both intra- and inter-molecular reactions and even activate the sp^3 bonds of $SiMe_4$. That these reactions occur under mild conditions with hydrocarbons of very low acidity is extraordinary for stable, isolatable complexes.

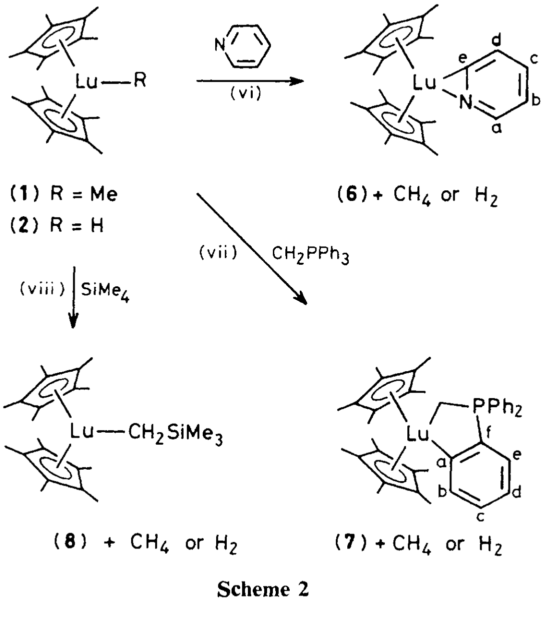
The hydride Lu(η^5-C_5Me_5)$_2$H (**2**) [$\nu_{\mathrm{Lu-H}}$(Nujol) 1345 cm^{-1}] is readily formed†[1] by hydrogenolysis of (**1**) [reaction (i), Scheme 1; pentane solution, 20 °C, 1 atm H_2]. This hydride rapidly undergoes H/D exchange when dissolved in deuteriated arenes [benzene or toluene, reaction (ii)] at 20 °C forming the deuteride, Lu(η^5-C_5Me_5)$_2$D [$\nu_{\mathrm{Lu-D}}$(Nujol) 975 cm^{-1}]. As shown in reaction (ii), Scheme 1, exchange with D_2 also occurs in pentane at 20 °C.

A more important non-degenerate intermolecular C–H activation between the hydride (**2**) and benzene occurs [reaction (iii)] wherein hydrogen is liberated and the phenyl complex (**3**) is formed [360 MHz ^{1}H n.m.r. of (**3**) (C_6D_{12}) δ 1.84 (s, 30 H, C_5Me_5), 6.84 (d, J_{HH} 6.45 Hz, 2H, *o*-Ph), 6.98 (t, J_{HH} 7.6 Hz, 1H, *p*-Ph), and 7.14 (app.t, J_{HH} 7.3 Hz, 2H, *m*-Ph); ^{13}C n.m.r. C_6D_{12} δ 10.73 (C_5Me_5), 118.81 ($C_5\mathrm{Me}_5$), 125.01 (*p*-Ph) 126.94, 135.98 (*o*-Ph, *m*-Ph), and 198.54 p.p.m. (phenyl C–Lu)]. Reaction (iii) is rapidly reversible and formation of (**3**) plus H_2 is disfavoured thermodynamically. The reaction can be forced by purging H_2 from the solution or by coupling reactions (i) and (ii). Thus, a benzene solution of (**1**) and (**2**) (10:1) in a closed vessel is converted completely into (**3**) over several hours *via* coupled hydrogenolysis and metallation. [Methyl complex (**1**) does react directly with benzene but more slowly than the hydride (**2**).] A slower reaction of the phenyl group of (**3**) with hydride (**2**) (1:1 in hexane, 25 °C) gives the interesting *p*-metallated complex (**4**) [^{1}H n.m.r. of (**4**) (C_6D_{12}) δ 1.85 (s, 30H, C_5Me_5) and 6.60 (s, 4H, aryl); ^{13}C n.m.r. (C_6D_6) δ 10.57 (C_5Me_5), 117.7 ($C_5\mathrm{Me}_5$), 134.87 (aryl CH), and 194.78 p.p.m. (aryl C–Lu)]. Complex (**4**) is the only doubly metallated isomer formed, presumably for steric reasons.



Scheme 1

Co-ordination of Lewis bases to the hydride (**2**) inevitably results in further activation of the ligand [reactions (v), (vi), and (vii), Schemes 1 and 2]. The diethyl ether adduct of (**2**),[2] stable below −30 °C, extrudes ethane on warming to give Lu(η^5-C_5Me_5)$_2$OEt, (**5**) [^{1}H n.m.r. of (**5**) (C_6D_6) δ 1.42 (t, J_{HH} 7.06 Hz, 3H, CH_3), 2.04 (s, 30H, C_5Me_5), 4.46 (q, J_{HH} 7.06 Hz, 2H, CH_2); ^{13}C n.m.r. (C_6D_6) δ 11.53 (C_5Me_5), 22.19 (CH_3), 62.28 (O-CH_2), and 116.13 p.p.m. ($C_5\mathrm{Me}_5$)]. Only C_2HD_5 is observed when $(C_2D_5)_2O$ is used suggesting a direct attack of hydride on the carbon α to oxygen, and not a possible mechanism involving initial metallation at the β-carbon atom.



Scheme 2

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† All the lutetium complexes reported in this communication are isolated as white crystalline solids or powders, characterised by full elemental analyses, i.r. spectra, and hydrolysis experiments in addition to the n.m.r. data reported in the text. N.m.r. data for (**1**) and (**2**) are in ref. 1.

Co-ordination of pyridine to (**1**) or (**2**) gives initial adducts (**1**)·pyridine or (**2**)·pyridine and is followed by metallation at the 2-position of pyridine with concomitant evolution of H_2 or CH_4. The structure of the product (**6**) (from *X*-ray crystallography[3]) shows the *o*-metallated pyridine ring to lie in the plane between the two η^5-C_5Me_5 rings, with both C and N co-ordinated to the Lu atom [^1H n.m.r. of (**6**) (C_6D_{12}) δ 1.75 (s, 30H, $C_5\mathit{Me}_5$), 6.89 (ddd, 1H, H_b), 7.32 (td, 1H, H_c), 7.73 (dt, 1H, H_d), 8.23 (dt, 1H, H_a) ($J_{bc} = J_{cd} = 7.36$ Hz; $J_{ab} = 5.12$ Hz; $J_{ac} = J_{ad} = J_{bd} = 1.4$ Hz); ^{13}C n.m.r. (C_6D_{12}) δ 10.45 ($C_5\mathit{Me}_5$), 115.88 (C_5Me_5), 120.82 (C_b), 133.43 and 133.81 (C_c,C_d), 145.3 (C_a), and 234.26 p.p.m. (C_e)]. The kinetics of formation of (**6**) are first order in (**1**)·pyridine adduct but show virtually no dependence on the excess of pyridine, suggesting an intramolecular reaction. Interestingly a similar *o*-metallation reported for $Ti(C_5H_5)_2R$ complexes only occurs with 2-substituted pyridines, not with pyridine itself.[4]

Further examples of intramolecular aryl C–H activation, but now at the δ-position, are observed with ylide complexes. Addition of CH_2PPh_3 to (**1**) or (**2**) gives initial adducts (**1**)·CH_2PPh_3 and (**2**)·CH_2PPh_3 which then eliminate CH_4 or H_2 (respectively) at 20 °C in toluene or pentane to give the 5-membered metallacycle, (7) (Scheme 2) [^1H n.m.r. of (7) (C_6D_6) δ 0.49 (d, 2H, Lu–CH_2–P, $J_{PH} = 14.5$ Hz), 1.99 (s, 30H, $C_5\mathit{Me}_5$), 6.95—7.05 (m, 7H, *m*-Ph, *p*-Ph, and H_d at 7.03, by decoupling) 7.29 (td, 1H, H_e, $J_{ed} = J_{PH} = 8.5$ Hz, $J_{ce} = 1.1$ Hz) 7.36 (tdd, 1H, H_c, $J_{cb,cd} = 7.3$ Hz, $J_{ce} = 1.1$ Hz, $J_{PH} = 2.8$ Hz), 7.62 (m, 4H, *o*-Ph, $J_{HH} = 6.5$, 1.5 Hz, $J_{PH} = 13.2$ Hz), and 7.7 (d, 1H, H_b, $J_{bc} = 7.3$ Hz)].

Intermolecular reaction of tetramethylsilane with (**1**) [reaction (viii), Scheme 2; 40 °C in cyclohexane] again results in metallation and clean elimination of methane (1 equiv.) to form complex (**8**) in high yield [^1H n.m.r. of (**8**) (C_6D_{12}) δ −0.39 (s, 2H, Lu–CH_2), −0.03 (s, 9H, $SiMe_3$), 1.98 (s, 30H, $C_5\mathit{Me}_5$); ^{13}C n.m.r. (C_6D_6) δ 4.8 ($SiMe_3$), 11.5 ($C_5\mathit{Me}_5$), 22.96 (Lu–CH_2), and 118.54 p.p.m. (C_5Me_5)]. For R = H rather than CH_3, reaction (viii) is readily reversible and the hydride (**2**) is thus a catalyst for the H/D exchange between tetramethylsilane and D_2 or C_6D_6. Precedents for intramolecular activation of silyl–methyl C–H groups exist in uranium chemistry.[5,6] Other examples of such ready intermolecular activation of tetramethylsilane are uncommon.[7,8] Organolanthanide complexes containing the CH_2SiMe_3 ligand have been prepared,[9,10] however, by metathetical routes.

In conclusion, the reactions described demonstrate the following important points. C–H activation is a general phenomenon for both lanthanide alkyls and lanthanide hydrides. The alkyls and hydrides, while stable and isolatable, show a remarkable level of reactivity; however, this reactivity can be quite selective giving high yields of a single product. Finally, the products of these C–H activation reactions are interesting complexes themselves and not necessarily easily prepared by other routes.

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References

1 P. L. Watson and D. C. Roe, *J. Am. Chem. Soc.*, 1982, **104**, 6471.

2 P. L. Watson, *J. Am. Chem. Soc.*, 1982, **104**, 337.

3 J. Calabrese and P. L. Watson, in preparation.

4 E. Klei and J. H. Teuben, *J. Organomet. Chem.*, 1981, **214**, 53.

5 J. W. Bruno, T. J. Marks, and V. W. Day, *J. Am. Chem. Soc.*, 1982, **104**, 7357.

6 S. J. Simpson, H. W. Turner, and R. A. Andersen, *Inorg. Chem.*, 1981, **20**, 2991.

7 Tetramethylsilane does react with the photolysis product of $W(\eta^5$-$C_5H_5)_2H_2$: M. Berry, K. Elmitt, and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1979, 1950.

8 M. F. Lappert, L. M. Engelhardt, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1982, 1323, and references therein.

9 H. Schumann, W. Genthe, N. Bruncks, and J. Pickardt, *Organometallics*, 1982, **1**, 1194, and references therein.

10 J. L. Atwood, W. E. Hunter, R. D. Rogers, J. Holton, J. McKeeking, R. Pearce, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1978, 140.