Selective Alkane C–C Bond Cleavage *via* Prior Dehydrogenation by a Transition Metal Complex

Robert H. Crabtree* and Robert P. Dion

Yale Chemistry Department, 225 Prospect Street, New Haven, CT 06520, U.S.A.

1,1-Dimethylcyclopentane is dehydrogenated to form $[(\eta^4\text{-}C_5H_4Me_2)IrL_2]^+$ [L = $(p\text{-}FC_6H_4)_3P$] and then rearranged to give $[(\eta^5\text{-}C_5H_4Me)Ir(Me)L_2]^+$ by $[IrH_2(Me_2CO)_2L_2]^+$, the first case of homogeneous C–C bond cleavage starting from an alkane with a transition metal complex.

Our interest in the co-ordination chemistry of alkanes[1] has led us to look for ways of selectively breaking C–C bonds with a transition metal complex. We have been unable to do this in one step, but have developed a two-step route (Scheme 1), involving prior dehydrogenation, followed by alkyl migration.[2]

Neat 1,1-dimethylcyclopentane† (**1**) reacts with $[IrH_2(Me_2CO)_2\{(p\text{-}FC_6H_4)_3P\}_2]SbF_6$ (**2**) and t-butylethylene (tbe) at 150 °C over 8 h to give, among other products, a 5,5-dimethylcyclopentadiene complex (**3**) (50%). As in our earlier dehydrogenation of alkanes,[3] tbe acts as hydrogen acceptor in this reaction. The identity of the deep red product (**3**) was determined by independent synthesis from (**2**) and neat 5,5-dimethylcyclopentadiene[4] (85 °C; 2 h) and from microanalytical and spectral data.‡ In particular, the two methyl groups, *endo* and *exo*, appear at δ 0.82 and 1.62 in the

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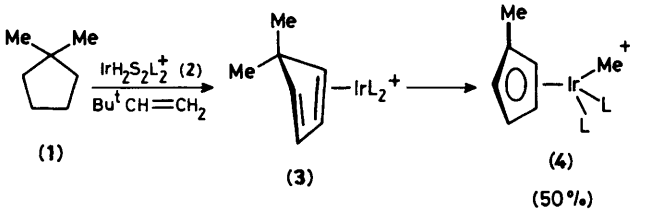
† 1,1-Dimethylcyclopentane (labelled as 99.993% pure) was supplied by the American Petroleum Institute, Carnegie Mellon University. No dimethylcyclopentenes (<0.01%) were detected by g.c. The reactions were carried out in a resealable 5 ml glass pressure vessel *in vacuo* with 0.4 ml of hydrocarbon, 100 μl (0.77 mmol) of tbe, and 100 mg (0.11 mmol) of metal complex. Products were detected and quantified by ^{1}H n.m.r. spectroscopy (90 or 500 MHz) and characterised by spectral and analytical data. The reactions do not involve metallic Ir, as judged by the usual tests (ref. 4; D. R. Anton and R. H. Crabtree, *Organometallics*, 1983, **2**, 855). In particular, the yields are unaffected by the presence of metallic Hg.

‡ N.m.r. data, for solutions in $(CD_3)_2CO$: (**3**), ^{1}H, δ 0.82 (s, Me), 1.62 (s, Me), 4.2 and 5.6 (each m, cyclopentadiene), and 7.08—7.96 (m, ArH); (**4**), ^{1}H, δ 1.45 (t, *J* 5.5 Hz, IrMe), 1.83 (m, Me), 5.04 and 5.50 (m, cyclopentadiene), and 6.95—7.48 (m, ArH); ^{1}H decoupled ^{13}C, δ −27.7 (t, *J* 5.5 Hz, IrMe), 15.5 (s, $\mathit{Me}C_5H_4$), 88.4 and 91.2 (s, =CH–), 112.1 (s, $Me\mathit{C}C_4H_4$), and 116.5 (m), 128.3 (d, *J* 32 Hz), 136.2 (s), and 164.0 (d, *J* 123 Hz) (all ArC); $[Ir(C_5H_5Me)HL_2]SbF_6$, ^{1}H, δ −14.59 (t, *J* 28.8 Hz, IrH), 1.90 (m, Me), 5.26 and 5.5 (m, cyclopentadiene), and 7.02—7.78 (m, ArH) ($\nu_{max.}$ 2160 cm^{-1}, Ir–H); (**6**), ^{1}H, δ −9.84 (t, *J* 26 Hz, IrH), 0.52 (s, Me), 1.40 (s, Me), 2.95 (d, *J* 5.4 Hz, 1- and 5-H), 4.68 (t, *J* 4.5 Hz, 2- and 4-H), and 7.12—7.84 (m, 3-H and ArH) ($\nu_{max.}$ 2160 cm^{-1}, Ir–H); $[Ir(toluene)L_2]SbF_6$, ^{1}H, 2.40 (s, Me), 5.61 (d, *J* 3.6 Hz, *o*-H), 5.84 (t, *J* 6.3 Hz, *m*-H), and 6.64—7.72 (m, *p*-H and ArH).

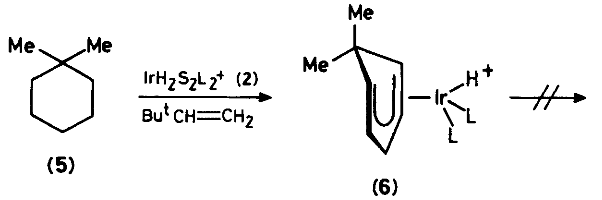


Scheme 1. S = Me_2CO; L = $(p\text{-}FC_6H_4)_3P$.

^1H and at δ 24.6 and 37.1 in the ^{13}C n.m.r. spectrum. For both methyl groups, the ^1J (^{13}C, ^1H) coupling constants are 127 Hz and so we do not suspect any CH ··· Ir bridging in this 16-electron cation.[5]

Also present in the reaction mixture from 1,1-dimethylcyclopentane is another product $[Ir(C_5H_4Me)(Me)L_2]SbF_6$ (**4**)‡ (~5% *initially* present). Further heating leads to an increase in the yield of (**4**) at the expense of (**3**). Ultimately, after a further 12 h, only (**4**) is observed, in 50% yield based on (**2**). That (**4**) arises from the diene complex (**3**) was verified by heating crystalline (**3**) (prepared from the neat diene; 85 °C for 2 h) at 145 °C for 18 h *in vacuo* to give (**4**) quantitatively. In (**4**), the methyl group bonded to the metal shows a triplet [^3J(P,H) 5.5 Hz] at δ 1.45 and a narrow multiplet at δ 1.83 which we assign to a methylcyclopentadienyl group; $[Ir(C_5H_4Me)HL_2]SbF_6$, prepared from 1-methylcyclopentene and (**2**), has a similar *M*e-cyclopentadiene resonance, probably owing to long-range coupling.

3,3-Dimethylcyclohexane (**5**)§ also reacts with (**2**) and tbe at 145 °C for 24 h to give the 6,6-dimethylcyclohexadienyl compound $[Ir(C_6H_5Me_2)HL_2]SbF_6$ (**6**) (Scheme 2). Complex (**6**) can also be prepared from 3,3-dimethylcyclohexene (neat) and (**2**) (85 °C; 2 h). Once again the *exo* and *endo* methyl groups are distinct in the ^1H n.m.r. spectrum at δ 1.40 and 0.52. Heating under the same conditions that converted (**3**) into (**4**) has no effect on (**6**), suggesting that an open co-ordination site, available in (**3**) but not in (**6**), may be required for C–C cleavage. The toluene complex $[Ir(toluene)L_2]SbF_6$‡ is not formed in this reaction, but would have been observed if present, as verified by independent synthesis from toluene, tbe, and (**2**), at 85 °C for 2 h.



Scheme 2

We conclude that C–C bond cleavage in alkanes can be brought about by a transition metal metal complex, but that C–H bond breaking[3,6] may generally precede C–C cleavage. Mechanistically, a concerted C–C cleavage is most likely; experiments on this question are in hand. Just as alkane C–H activation is difficult partly because M–C bonds tend to be weak,[7] direct alkane C–C activation is probably even less favourable. In our case, however, prior C–H activation leads to a situation in which the breaking of the C–C and formation of the M–C bonds is driven by the aromatisation the C_5 ring. This emphasizes the importance of the availability of *multiple* sites of co-ordinative unsaturation[4] [*e.g.*, by loss of Me_2CO and H from (**2**)] in alkane C–C bond activation.

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§ Aldrich, used as received. Absence (<0.01%) of dimethylcyclohexenes verified by g.c.