Enantioselective Alkylating Reagents; Crystal Structure of $[Ru\{\eta^5\text{-}C_5H_4(C_{10}H_{19})\}(dppe)(IEt)]CF_3SO_3$ [dppe = $PPh_2CH_2CH_2PPh_2$, $C_{10}H_{19}$ = (+)-neomenthyl]

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The complex $[Ru\{\eta^5\text{-}C_5H_4(C_{10}H_{19})\}(dppe)I]$ **1** [dppe = $PPh_2CH_2CH_2PPh_2$, $C_{10}H_{19}$ = (+)-neomenthyl] reacts with CF_3SO_3R (R = Me or Et) to give the corresponding alkyl iodide complexes $[Ru\{\eta^5\text{-}C_5H_4(C_{10}H_{19})\}(dppe)(IR)]$ CF_3SO_3 (R = Me **2a** or Et **2b**) which alkylate a range of prochiral nucleophiles (e.e. ≤20%) to regenerate **1**; the crystal structure of **2b** is reported.

In recent years several transition-metal complexes containing an alkyl halide ligand coordinated *via* the halide have been synthesised;[1,2] most have been generated and characterised in solution although the X-ray crystal structures of some have been reported.[3] Stimulated by reports[2c,d] that coordination markedly activates the alkyl halide towards nucleophilic attack {*e.g.* $[Ir(H)_2(PPh_3)_2(IMe)_2]PF_6$ methylates hindered amines *ca.* 10^6 times faster than does free iodomethane[2c]} we initiated a programme to synthesise chiral transition-metal complexes containing an alkyl halide ligand which could be used to enantioselectively alkylate a range of organic nucleophiles. Our preliminary results are described herein.

$[Ru\{\eta^5\text{-}C_5H_4(C_{10}H_{19})\}(dppe)I]$ **1** [dppe = $PPh_2CH_2CH_2PPh_2$ $C_{10}H_{19}$ = (+)-neomenthyl] is a yellow air-stable complex which is readily prepared optically pure in 62% yield from $[Ru_3(CO)_{12}]$ without the need for resolution.[4] This complex reacts with CF_3SO_3R (R = Me or Et) to give the corresponding alkyl iodide complexes $[Ru\{\eta^5\text{-}C_5H_4(C_{10}H_{19})\}(dppe)(IR)]CF_3SO_3$ (R = Me **2a**, 76%; R = Et **2b**, 96%). Both have been isolated analytically pure and fully characterised;† although stable, both are best stored in the freezer under nitrogen. Attempts to grow crystals of **2a** suitable for X-ray crystallography were unsuccessful although **2b** readily yielded orange-red oblong crystals.‡ The complex **2b** is one of the few ethyl iodide complexes reported and the first to be structurally characterised (Fig. 1). The Ru–I bond distance 2.676(3) Å is, within experimental error, the same as that found in $[Ru(\eta^5\text{-}C_5H_5)(CNBu^t)(PPh_3)(IMe)]PF_6$[3c] but significantly shorter than Ru–I terminal bonds which are normally in the range 2.72–2.78 Å.[2e] Similarly the CH_2–I bond distance, 2.064(24) Å, is considerably shorter than the 2.139 Å found in free ethyl iodide;[5] this contrasts with previous structures of alkyl halide complexes where a slight increase in the C–I bond has been found.[3b] Curiously the CH_3–CH_2 bond, 1.415(47) Å is also shorter than that associated with C–C single bonds.

A particularly attractive feature of **2b** is that the phenyl groups of the bis(diphenylphosphino)ethane ligands extend towards the cyclopentadienyl ring forcing the bulky chiral

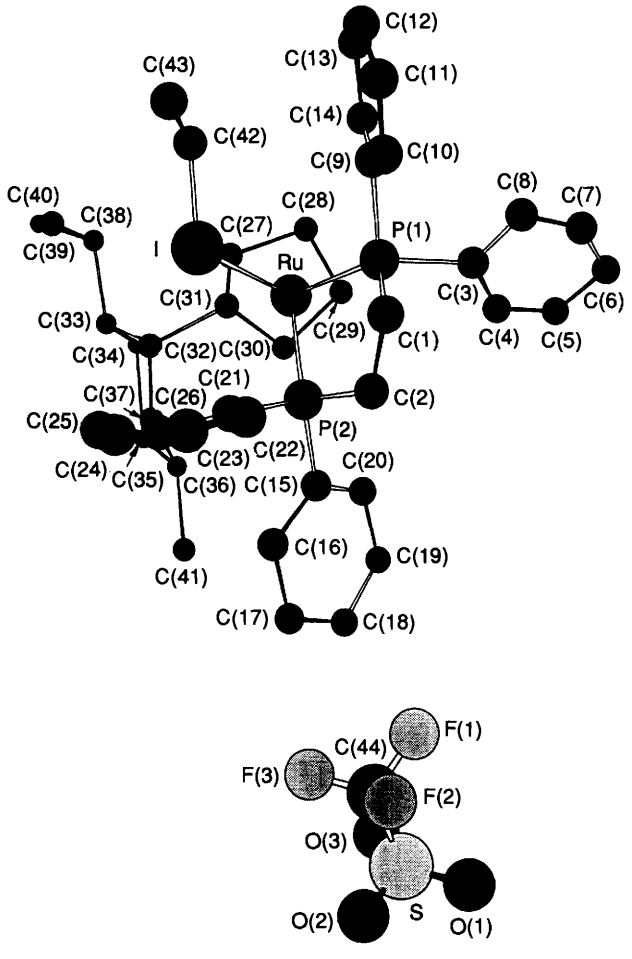
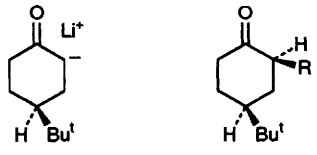
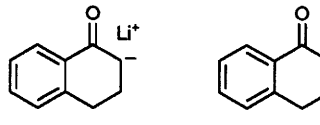
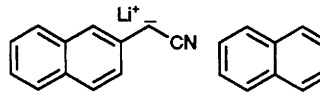
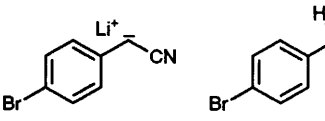


Fig. 1 Structure of $[Ru\{\eta^5\text{-}C_5H_4(C_{10}H_{19})\}(dppe)(IEt)]CF_3SO_3$ **2b**. Selected bond lengths (Å) and angles (°): Ru–I 2.676(3), I–C(42) 2.064(24), C(42)–C(43) 1.415(47), Ru–P(1) 2.277(5), Ru–P(2) 2.330(6), C(27)–C(28) 1.365(31), C(28)–C(29) 1.460(31), C(29)–C(30) 1.378(26), C(30)–C(31) 1.375(35), C(27)–C(31) 1.393(29), Ru–I–C(42) 107.3(7), I–C(42)–C(43) 114.0(21), I–Ru–P(1) 92.0(1), I–Ru–P(2) 89.5(2), P(1)–Ru–P(2) 83.8(2).

Table 1 Alkylations carried out using $[Ru\{\eta^5\text{-}C_5H_4(C_{10}H_{19})\}(dppe)(IR)]CF_3SO_3$

Substrate	Product	R = Me	R = Et
		28.0% d.e.[b]	8.0% d.e.[b]
		20.0% e.e.[c]	6.0% e.e.[c]
		19.5% e.e.[c]	20.0% e.e.[c]
		15.3% e.e.[b]	8.5% e.e.[b]

[a] Carried out in CH_2Cl_2–THF at −78 °C using 0.1 mmol of **2a** or **2b**. [b] Measured by chiral GC using Cyclodex B. [c] Measured by chiral HPLC using Chiralcel-OD.

substituent to adopt a position above the alkyl halide ligand. Consequently, the neomenthyl substituent is in a position to influence the stereoselectivity of nucleophilic attack upon the alkyl halide ligand; that it does so is clearly indicated by the results given in Table 1. The organometallic product of the alkylations is the original iodide complex **1** which is readily recovered and recycled; thus, the alkylations are catalytic with respect to the chiral ruthenium complex. It must be stressed that the optical yields have yet to be optimised but given the recognised difficulty of obtaining high e.e. from asymmetric catalytic alkylation reactions[6] these initial results are encouraging, as is the fact that stereoselectivity is observed with a wide range of nucleophiles.

Summarising, we have demonstrated that chiral transition-metal alkyl halide complexes may effect asymmetric alkylation of prochiral nucleophiles. Work is in progress to develop such complexes into highly enantioselective catalysts.

Financial support from the SERC is gratefully acknowledged.

Received, 14th October 1993; Com. 3/06161B

Footnotes

† *Selected spectroscopic data* (*J*/Hz): [Ru{η^5-C_5H_4($C_{10}H_{19}$)}(dppe)I] **1**: δ_H (250 MHz, $CDCl_3$) 8.10–6.90 (20H, m, Ph), 5.31, 4.75, 3.90, 3.75 (4H, s, C_5H_4), 3.05 (1H, br s, 5-H of $C_{10}H_{19}$), 3.00–2.10 (2H, m, CH_2 of dppe), 2.00 (1H, d, *J* 13.0, $C_{10}H_{19}$), 1.90–1.05 (10H, m, 8H of $C_{10}H_{19}$ merging with 2H of dppe), 0.95 (3H, d, *J* 6.5, CH_3 of $C_{10}H_{19}$), 0.85 (3H, d, *J* 6.5, CH_3 of $C_{10}H_{19}$), 0.75 (3H, d, *J* 6.5, CH_3 of $C_{10}H_{19}$); $\delta_C\{^1H\}$ (100 MHz, CD_2Cl_2) 134.8–127.8 (24C, m, Ph), 107.5 (1C, d, J_{PC} 10.1, C_5H_4), 85.3 (1C, s, C_5H_4), 80.6 (1C, s, C_5H_4), 77.8 (1C, s, C_5H_4), 72.8 (1C, s, C_5H_4), 50.3 (1C, s, C-38), 40.7 (1C, s, C-37), 36.4 (1C, s, C-32), 36.1 (1C, s, C-35), 29.5 (1C, s, C-36), 29.2 (dd, 1C, CH_2 of dppe), 28.7 (1C, s, C-38), 27.5 (1C, dd, CH_2 of dppe), 24.7 (1C, s, C-34), 22.9 (1C, s, C-41),* 22.7 (1C, s, C-39),* 21.0 (1C, s, C-40)*; $\delta P\{^1H\}$ (101 MHz, $CDCl_3$, ref. H_3PO_4) P_A 79.5, P_B 75.4 (AB q, $J_{P_AP_B}$ 20.7).

[Ru{η^5-C_5H_4($C_{10}H_{19}$)}(dppe)(IMe)] CF_3SO_3 **2a**: δ_H (250 MHz, CD_2Cl_2) 8.10–7.75 (20H, m, Ph), 5.24, 4.77, 4.74, 4.27 (4H, s, C_5H_4), 2.80 (1H, s, 5-H of $C_{10}H_{19}$), 3.05–2.45 (4H, m, 2 × CH_2 of dppe), 2.40–1.00 (9H, m, $C_{10}H_{19}$), 1.15 (3H, s, ICH_3), 0.95 (3H, d, *J* 6.5, CH_3 of $C_{10}H_{19}$), 0.89 (3H, d, *J* 6.5, CH_3 of $C_{10}H_{19}$), 0.80 (3H, d, *J* 6.5, CH_3 of $C_{10}H_{19}$); $\delta_C\{^1H\}$ (62.9 MHz, CD_2Cl_2) 137.6–129.3 (24C, m, Ph), 113.8 (1C, s, C-31 of C_5H_4), 87.1 (1C, s, C_5H_4), 85.2 (1C, d, J_{PC} 4.9, C_5H_4), 81.5 (1C, s, C_5H_4), 80.3 (1C, d, J_{PC} 7.1, C_5H_4), 53.9 (1C, s, C-33), 53.3 (1C, s, C-32), 49.6 (1C, s, C-36), 40.4 (1C, s, C-37), 36.3 (1C, s, C-38), 35.2 (1C, s, C-35), 29.2 (1C, s, C-39),* 28.8 (1C, s, C-40),* 27.1 (2C, m, 2 × CH_2 of dppe), 22.8 (1C, s, C-41),* 22.7 (1C, s, C-11), −12.6 (1C, s, ICH_3); $\delta P\{^1H\}$ (101 MHz, CD_2Cl_2, ref. H_3PO_4) P_A 76.9, P_B70.7 (AB q, $J_{P_AP_B}$ 27.6); $\delta_F\{^1H\}$ (235 MHz, CD_2Cl_2, ref. $CFCl_3$) −78.8 (s).

[Ru{η^5-C_5H_4($C_{10}H_{19}$)}(dppe)(IEt)] CF_3SO_3 **2b**: δ_H (250 MHz, CD_2Cl_2) 8.00–6.85 (20H, m, Ph), 5.21, 4.82, 4.72, 4.22 (4H, s, C_5H_4), 3.00–2.15 (4H, overlapping m, 2 × CH_2 of dppe), 2.75 (1H, br s, 5-H of $C_{10}H_{19}$), 2.05 (1H, dq, *J* 7.5, $IC\mathit{H}_a\mathit{H}_bCH_3$), 1.95 (1H, dq, *J* 7.5, $ICH_a\mathit{H}_bCH_3$), 1.90–1.05 (9H, m, $C_{10}H_{19}$), 1.00 (3H, t, *J* 7.5, $ICH_2C\mathit{H}_3$), 0.95 (3H, d, *J* 6.5, CH_3 of $C_{10}H_{19}$), 0.85 (3H, d, *J* 6.5, CH_3 of $C_{10}H_{19}$), 0.75 (3H, d, *J* 6.5, CH_3 of $C_{10}H_{19}$); $\delta_C\{^1H\}$ (62.9 MHz, CD_2Cl_2) 137.0–128.4 (24C, m, Ph), 113.7 (1C, s, C-31 of C_5H_4), 85.3 (1C, d, J_{PC} 4.8, C_5H_4), 81.4 (1C, s, C_5H_4), 79.8 (1C, s, C_5H_4), 70.7 (1C, s, C_5H_4), 54.9 (1C, s, C-33), 54.3 (1C, s, C-32), 49.6 (1C, s, C-36), 40.3 (1C, s, C-37), 36.4 (1C, s, C-38), 35.1 (1C, s, C-35), 29.1 (1C, s, C-39),* 28.8 (1C, s, C-40), 27.0 (2C, m, 2 × CH_2 of dppe), 24.1 (1C, s, C-34), 22.8 (1C, s, C-41),* 19.1 (1C, s, $ICH_2\mathit{C}H_3$), 12.6 (1C, s, $I\mathit{C}H_2CH_3$); $\delta_P\{^1H\}$ (101 MHz; CD_2Cl_2, ref. H_3PO_4) P_A 76.5, P_B 70.4 (AB q, $J_{P_AP_B}$ 27.8 Hz); $\delta F\{^1H\}$ (235 MHz, CD_2Cl_2, ref. $CFCl_3$) −78.7 (s). (* these assignments may be interchanged). Carbon atom numbering follows that assigned in the crystal structure.

‡ *Crystal data*: **2b**, $C_{44}H_{52}F_3IO_3P_2RuS$; M = 1007.88; crystallises from dichloromethane–iodoethane–*n*–hexane as orange-red oblongs (0.60 × 0.30 × 0.20 mm); monoclinic, space group $P2_1$ (C_2^2, no. 4), a = 11.842(11), b = 15.306(9), c = 11.991(6) Å, β = 95.57(6)°, U = 2163(3) Å^3, Z = 2, D_c = 1.548 g cm^{-3}, μ(Mo-Kα) = 12.30 cm^{-1}, F(000) = 1019.91. Intensity data collected at room temperature on a Nicolet R3 diffractometer Mo-Kα radiation (λ = 0.710 69 Å). R = 0.0666 (2229 reflections).

Atomic coordinates, bond lengths and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 R. J. Kulawiec and R. H. Crabtree, *Coord. Chem. Rev.*, 1990, **99**, 89.

2 (*a*) D. N. Lawson, J. A. Osborn and G. Wilkinson, *J. Chem. Soc. A*, 1966, 1733; (*b*) C. H. Winter, A. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1987, **109**, 7560. (*c*) C. H. Winter and J. A. Gladysz, *J. Organomet. Chem.*, 1988, **354**, C33; (*d*) R. J. Kulawiec and R. H. Crabtree, *Organometallics*, 1988, **7**, 1891; (*e*) R. J. Kulawiec, J. W. Faller and R. H. Crabtree, *Organometallics*, 1990, **9**, 745; (*f*) A. Igau and J. A. Gladsyz, *Polyhedron*, 1991, **10**, 1903; (*g*) P. F. Yang and G. K. Yang, *J. Am. Chem. Soc.*, 1992, **114**, 6937.

3 (*a*) M. J. Burk, B. Segmuller and R. H. Crabtree, *Organometallics*, 1987, **6**, 2241; (*b*) C. H. Winter, W. R. Veal, C. M. Garner, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1989, **111**, 4766; (*c*) F. M. Conroy-Lewis, A. D. Redhouse and S. J. Simpson, *J. Organomet. Chem.*, 1989, **366**, 357; (*d*) M. R. Colsman, T. D. Newbound, L. J. Marshall, M. D. Noirot, M. M. Miller, G. P. Wulfsberg, J. S. Frye, O. P. Anderson and S. H. Strauss, *J. Am. Chem. Soc.*, 1990, **112**, 2349; (*e*) M. Bown and J. M. Waters, *J. Am. Chem. Soc.*, 1990, **112**, 2442; (*f*) A. Igau and J. A. Gladysz, *Organometallics*, 1991, **10**, 2327; (*g*) D. M. Van Seggen, O. P. Anderson and S. H. Strauss, *Inorg. Chem.*, 1992, **31**, 2987; (*h*) J. Powell, M. Horvath and A. Lough, *J. Chem. Soc., Chem. Commun.*, 1993, 733.

4 Synthesised by the method described in E. Cesarotti, L. Prati, A. Sironi, G. Ciani, and C. White, *J. Chem. Soc., Dalton Trans.*, 1987, 1149.

5 T. Kasuya and T. Oka, *J. Phys. Soc Jpn.*, 1960, **15**, 296.

6 A. Q. Mi, Z. Y. Wang and Y. Z. Jiang, *Tetrahedron Asymmetry*, 1993, **4**, 1957; M. J. O'Donnell, W. D. Bennett and S. Wu, *J. Am. Chem. Soc.*, 1989, **111**, 2353; E. V. Dehmlow, P. Singh and J. Heider, *J. Chem. Res. (S)*, 1981, 292.