

Uranium Pinacولات as Intermediates in the Reductive Coupling of Ketones; X-Ray Crystal Structure of a thf Solvate of the Uranium Bisbenzopinacolate $U(Ph_4C_2O_2)_2(thf)_2$ (thf = tetrahydrofuran)

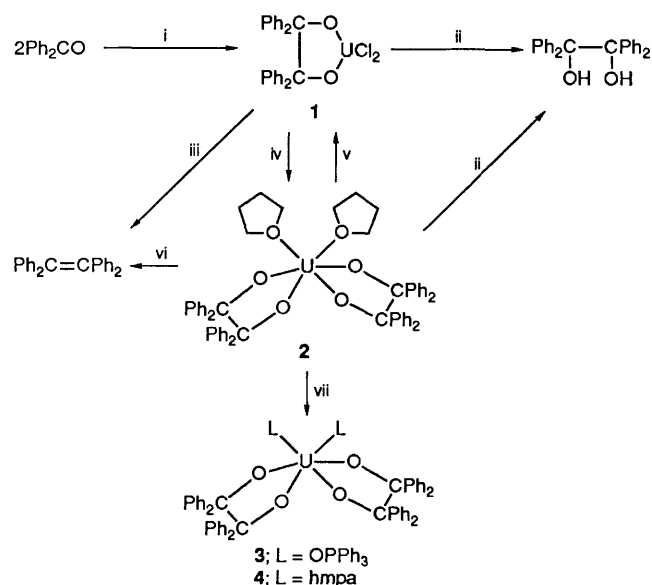
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The uranium benzopinacولات $U(Ph_4C_2O_2)Cl_2$ **1** and $U(Ph_4C_2O_2)_2(thf)_2$ **2** were isolated from the reaction of benzophenone with UCl_4 and $Na(Hg)$ and gave benzopinacol by hydrolysis or tetraphenylethylene after treatment with sodium amalgam; complex **2** adopts a distorted *cis*-octahedral configuration in the solid state.

Reductive coupling of ketones into diols or alkenes is a reaction of considerable interest which is mediated by low valent metallic species; titanium compounds are particularly effective in these transformations (*cf.* the McMurry alkene synthesis).¹ The mechanism of these reductions is controversial but it is well accepted that metalpinacولات are implied as intermediates. However, it is only from the reactions of $Ti(C_5H_5)_2(thf)_2$ (X = Cl, Br; thf = tetrahydrofuran) and $Ti(C_5H_5)_2(CO)_2$ ³ with organic carbonyl compounds that such metalpinacولات have been isolated, and no alkenes were obtained from these derivatives. Here we report on (i) the efficient coupling of cyclohexanone into the corresponding pinacol and the formation of either benzopinacol or tetraphenylethylene from benzophenone, by using the new reducing system $UCl_4-Na(Hg)$; (ii) the isolation and characterization of the pinacolate intermediates $U(Ph_4C_2O_2)Cl_2$ **1** and $U(Ph_4C_2O_2)_2(thf)_2$ **2**; and (iii) the solid state structure of a thf solvate of **2**.

Cyclohexanone (108 μ l, 1.04 mmol) was reduced under argon by a mixture of UCl_4 (198 mg, 0.52 mmol) and 2% $Na(Hg)$ (2394 mg, 2.08 mmol Na) in dry thf (50 ml); after stirring for 15 h under reflux, the solution was decanted, evaporated to dryness and hydrolysis produced 1,1'-bicyclohexyl-1,1'-diol which was isolated as colourless crystals (67 mg, 65%)[†] after extraction with diethyl ether. Formation of cyclohexylidenecyclohexane was not observed, even with an excess of reducing agent; no intermediate could be unambiguously characterized by NMR spectroscopy.



Scheme 1 Reagents and conditions: i, UCl_4 , 2Na(Hg), 20 °C, 12 h; ii, H_2O , 20 °C; iii, 2Na(Hg), 20 °C, 24 h; iv, 2Ph₂CO, 2Na(Hg), 20 °C, 12 h; v, UCl_4 , 20 °C; vi, 2Na(Hg), 65 °C, 72 h; vii, OPPh₃ or hmpa, 20 °C; all reactions in thf

[†] All the organic products have been characterized by their melting point, their NMR spectra and by GS-MS analysis.

Benzophenone (386 mg, 2.12 mmol) reacted with UCl_4 (403 mg, 1.06 mmol) and $Na(Hg)$ (2436 mg, 2.12 mmol Na) in thf (50 ml) to give the metalpinacol $U(Ph_4C_2O_2)Cl_2$ **1** in 90% yield (Scheme 1); the mixture was stirred at 20 °C for 12 h and the solution, after filtration, partial evaporation and addition of pentane, deposited off-white microcrystals. Compound **1** was alternatively prepared by treating UCl_4 with 2 equiv. of the ketyl anion Ph_2C-O^- or by mixing UCl_3 with 2 equiv. of the ketone (NMR experiments). Similar reaction of Ph₂CO with UCl_4 and $Na(Hg)$ in the molar ratio 4 : 1 : 4 afforded pale green crystals of the bisbenzopinacolate derivative $U(Ph_4C_2O_2)_2(thf)_2$ **2** (70% yield). This latter was also obtained by treatment of **1** with 2 equiv. of benzophenone in the presence of 2 equiv. of sodium amalgam, and its comproportionation with UCl_4 gave back **1** in quantitative yield (NMR experiments). The thf ligands of **2** were readily displaced by a stoichiometric amount of OPPh₃ or hmpa (hexamethylphosphoramide), giving complexes **3** and **4** which were respectively isolated as pale yellow and pale pink crystals. Compounds **1-4**, which are unique examples of uranium diolate complexes, were characterized by their elemental analyses (C, H, P, N, Cl), their NMR spectra[‡] and, in the case of **2** and **4**, by their X-ray crystal structure.[§]

Hydrolysis of **1** and **2** led to the immediate and quantitative formation of benzopinacol and treatment of **1** with 2 equiv. of sodium amalgam afforded tetraphenylethylene as the major organic product (75% yield by NMR, 67% isolated yield). Complex **2** was much less easily reduced than **1** (see the conditions in Scheme 1); its reaction with $Na(Hg)$ also gave Ph₂C=CPh₂ (30% yield by NMR) and a not yet identified organometallic species. Metalpinacولات **1** and **2** were thus shown to be intermediates in the reductive coupling of

[‡] ¹H NMR spectroscopic data: δ (60 MHz, 30 °C, in [2H₈]thf except **4** in [2H₂]dichloromethane) **1**: 18.95 (8 H, d, *J* 7 Hz, *o*-Ph), 8.23 (4 H, t, *J* 7 Hz, *p*-Ph), 7.68 (8 H, t, *J* 7 Hz, *m*-Ph); **2**: 13.59 (16 H, br, *w*_{1/2} 20 Hz, *o*-Ph), 5.15 (24 H, br, *w*_{1/2} 10 Hz, *m*- and *p*-Ph); **3**: 13.40 (16 H, d, *J* 7 Hz, *o*-CPh), 6.53 (6 H, br, *w*_{1/2} 25 Hz, *p*-PPh), 5.96 (12 H, br, *w*_{1/2} 25 Hz, *m*-PPh), 5.65 (8 H, t, *J* 7 Hz, *p*-CPh), 5.15 (16 H, t, *J* 7 Hz, *m*-CPh), 0.5 (12 H, br, *w*_{1/2} 140 Hz, *o*-PPh); **4**: 11.31 (16 H, d, *J* 7 Hz, *o*-Ph), 6.30 (8 H, t, *J* 7 Hz, *p*-Ph), 5.76 (16 H, t, *J* 7 Hz, *m*-Ph), -3.90 (36 H, d, *J* 9 Hz, hmpa).

[§] Crystal data for **2**·thf: C₆₄H₆₄O₇U, monoclinic, space group *P*2₁/*c*, *a* = 17.772(3), *b* = 18.260(9), *c* = 16.680(3) Å, β = 92.06° (4), *V* = 5409.5(6) Å³, *Z* = 4, *D*_c = 1.453 g cm⁻³, μ = 28.954 cm⁻¹. Data were collected using an Enraf-Nonius CAD-4 diffractometer (Mo-*K* α radiation, λ = 0.71073 Å) in the range 4 < 2 θ < 40°. 5839 reflections were collected at 23 °C and 3446 reflections with *I* > 3 σ (*I*) were used after Lorentz polarisation, intensity decay (-26.8% after 61 h, linearly corrected), and empirical absorption corrections. The structure was solved by the heavy-atom method and refined by full-matrix least-squares (*F*). The U and O atoms were refined anisotropically; the hydrogen atoms were introduced in idealized positions and constrained to ride on their parent carbon atoms. Analytical scattering factors for neutral atoms were corrected for *f'* and *f''*. The final *R* values were *R* = 0.044 and *R*_w = 0.052 (*w* = 1). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

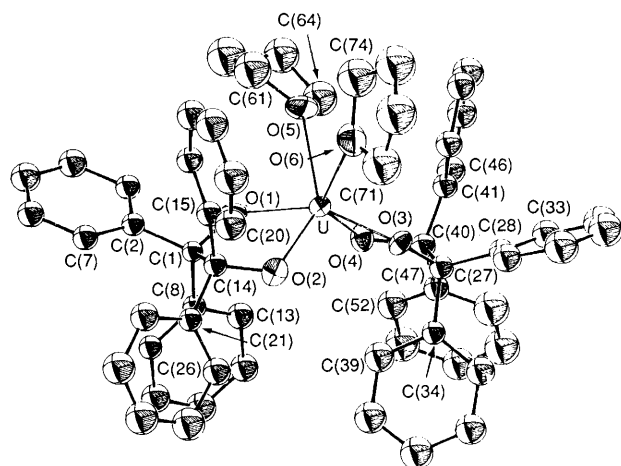


Fig. 1 The X-ray crystal structure of **2**·thf. Important distances (Å) and angles (°): U–O(1) 2.159(3), U–O(2) 2.162(4), U–O(3) 2.131(4), U–O(4) 2.158(3), U–O(5) 2.534(5), U–O(6) 2.558(4); O(1)–U–O(2) 70.5(1), O(3)–U–O(4) 70.1(1), O(5)–U–O(6) 76.6(2).

benzophenone into the α -diol or the alkene, that could be achieved at a preparative scale and in a 'one-pot' reaction by using the proper quantities of uranium tetrachloride and sodium amalgam. It is noteworthy that this reducing system is able to couple four molecules of benzophenone per uranium atom; this is in contrast to other transition metal systems where stoichiometry 1 : 1 carbonyl to metal centre is the rule,¹ and to active uranium or thorium powders which couple two aryl ketones per actinide atom.⁴ The selectivity of the UCl_4 –Na(Hg) system and its utility in the coupling of other carbonyl compounds is being studied.

Even though actinide alkoxides have been known for a long time,⁵ only the phenoxide derivatives $\text{U}(\text{OPh})_4$ -

($\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$)₂⁶ and $\text{U}(\text{O}-2,6\text{-Bu}^t_2\text{C}_6\text{H}_3)_4$ ⁷ have been crystallographically characterized; it was therefore of interest to determine the crystal structure of **2**·thf. It consists of discrete molecules which have a very distorted *cis*-octahedral geometry (Fig. 1). The angle distortions are caused by the small bite angle of the pinacolate ligands which are nearly 'isobidentate'.⁸ The U–O distances are unexceptional for tetravalent uranium complexes.⁵ Each five-membered chelate ring has one carbon atom, C(14) and C(40), which is out of the plane containing the four other atoms, at 0.64(1) and 0.46(1) Å, respectively; the dihedral angle between the two planes so defined is 67.3(4)°. The configuration of **4** is similar to that of **2**.⁹

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References

- 1 J. E. McMurry, *Acc. Chem. Res.*, 1983, **16**, 405; B. E. Kahn and R. D. Rieke, *Chem. Rev.*, 1988, **88**, 733; Y. Dang and H. J. Geise, *J. Organomet. Chem.*, 1991, **405**, 1.
- 2 R. S. P. Coutts, P. C. Wailes and R. L. Martin, *J. Organomet. Chem.*, 1973, **50**, 145; J. C. Huffman, K. G. Moloy, J. A. Marsella and K. G. Caulton, *J. Am. Chem. Soc.*, 1980, **102**, 3009.
- 3 M. Pasquali, C. Floriani, A. Chiesi Villa and C. Guastini, *Inorg. Chem.*, 1981, **20**, 349.
- 4 B. E. Kahn and R. D. Rieke, *Organometallics*, 1988, **7**, 463.
- 5 W. G. Van der Sluys and A. P. Sattelberger, *Chem. Rev.*, 1990, **90**, 1027.
- 6 P. G. Edwards, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1981, **103**, 7792.
- 7 W. G. Van der Sluys, A. P. Sattelberger, W. E. Streib and J. C. Huffman, *Polyhedron*, 1989, **8**, 1247.
- 8 D. L. Keppert, in *Inorganic Stereochemistry*, Springer Verlag, New York, 1982, ch. 7.
- 9 R. Adam, C. Villiers, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, unpublished results.