Deoxygenation of Carbon Monoxide by Triscyclopentadienyluranium Alkyl Complexes giving Alkylbenzene Molecules

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Carbon monoxide reacts with the alkyl complexes $[U(\eta^5\text{-}C_5H_5)_3R]$ in tetrahydrofuran to give, *via* the intermediacy of the acyl compounds $[U(\eta^5\text{-}C_5H_5)_3(\eta^2\text{-}COR)]$, the alkylbenzene molecules C_6H_5R (R = Me, Bu^n, Pr^i, Bu^t).

Much attention has been paid to η^2-acyl complexes of the lanthanide, actinide and early transition elements, *e.g.* $[Zr(C_5H_5)_2Me(\eta^2\text{-}COMe)]$[1] and $[Th(C_5Me_5)_2Cl(\eta^2\text{-}COMe)]$[2] because their structure and reactivity revealed unusual modes of CO activation. Many reactions of these derivatives, such as dimerisation, carbonylation or insertion into metal–hydrogen bonds, have been explained by their oxycarbene-like character.[1-3] De Boer and De With found that the acyl C–O bond of the labile titanium compound $[Ti(C_5Me_5)_2(\eta^2\text{-}COMe)]$ could be cleaved and they observed the formation of hexamethylbenzene, resulting from ring expansion of the C_5Me_5 ligand by incorporation of the acyl carbon atom.[4] Here we describe a similar transformation of the triscyclopentadienyluranium acyl complexes $[U(C_5H_5)_3(\eta^2\text{-}COR)]$ 1 leading to the corresponding alkylbenzene molecules C_6H_5R (Scheme 1), *via* deoxygenation of the acyl group and ring enlargement of a cyclopentadienyl ligand. This unusual reaction thus appears to be more general than might previously have been expected.

As described by Zanella *et al.*,[5] compounds 1 are readily synthesized by carbonylation of the alkyl complexes $[U(C_5H_5)_3R]$ (R = Me, Bu^n, Pr^i, Bu^t) in toluene; these acyl derivatives 1 could also be prepared in pentane or diethyl ether. However, on exposure to carbon monoxide (1 atm,

20 °C), a red solution of $[U(C_5H_5)_3Bu^n]$ (490 mg) in tetrahydrofuran (thf) (10 ml) deposited a brown powder; after 2 h, distillation of the pale-yellow solution afforded n-butylbenzene (25 mg, 20%).† Similar treatment of $[U(C_5H_5)_3Bu^n]$ with ^{13}CO showed that the carbon atom of the carbon monoxide was incorporated at the 1-position of the butylbenzene molecule. NMR spectroscopy showed that the acyl complex $[U(C_5H_5)_3(\eta^2\text{-}COBu^n)]$ was an intermediate in this reaction and that butylbenzene was the only organic product, formed in quantitative yield. In fact, complete formation of the aromatic molecule was observed within 10 min on dissolving $[U(C_5H_5)_3(\eta^2\text{-}COBu^n)]$ in tetrahydrofuran or by adding 1 equiv. of hexamethylphosphoramide to a solution of this complex in benzene (in the presence of 5% of the Lewis base, the reaction required 4 days for completion). Other acyl derivatives 1 (R = Me, Pr^i, Bu^t) behave similarly and gave

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† The alkylbenzene products were identified by comparison with authentical samples. Pure n-butylbenzene was identified by GC–MS, and ^1H and ^{13}C NMR spectroscopy; ^{13}C, δ (50 MHz, 30 °C in $CDCl_3$): 143.5 (*ipso* C), 128.9 (*ortho* and *meta* C), 126.2 (*para* C), 36.4, 34.4, 23.1 and 14.6 (butyl C). Cumene was also isolated and identified by its ^1H NMR spectrum whereas toluene and *tert*-butylbenzene were characterized in the reaction mixture by their NMR specta.
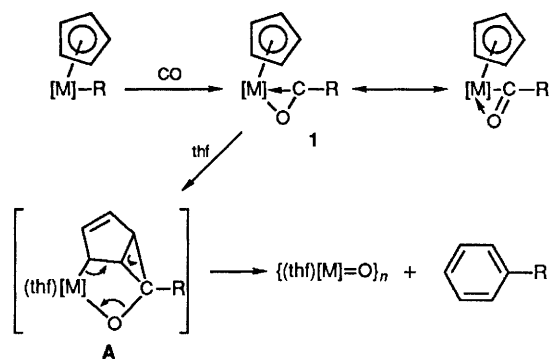
Scheme 1 [M] = U(C$_5$H$_5$)$_2$; R = Me, Bu^n, Pr^i, Bu^t

respectively toluene, cumene and *tert*-butylbenzene in quantitative yield.† Transformation of **1** in thf was much slower with the secondary and tertiary R groups and was achieved after 2 days. The rates of these reactions were not affected by varying the concentration of **1** (from 10^{-2} to 10^{-1} mol dm^{-3}), suggesting a monomolecular rearrangement process. The brown precipitate from each of the above reactions was insoluble in common organic solvents; a sample analysed reasonably satisfactorily for U(C$_5$H$_5$)$_2$O·thf.‡ Since its IR spectrum in Nujol did not exhibit any absorption corresponding to a U=O bond, a polymeric structure with U–O–U links, as found in the polymeric or trimeric forms of Zr(C$_5$H$_5$)$_2$O and Hf(C$_5$H$_5$)$_2$O,[6] is proposed.

It seems likely that the oxycarbenoid character of complexes **1** is responsible for their transformation. In coordinating solvents or in the presence of a Lewis base, the carbene species should be displaced from the metal and should attack

the cyclopentadienyl ligand, giving an intermediate or a transition state such as **A** in Scheme 1; pericyclic rearrangement of the latter should afford the final products.

Finally, we note that in the Fischer–Tropsch reaction, CO insertion into metal–alkyl species is generally considered as a chain termination step,[7] leading to oxygenated products, even if carbene or alkyl complexes could be obtained by treating acyl derivatives with metal hydride species.[3,8] This work shows that deoxygenation of acyl intermediates is a feasible process and provides an example of a new means for cleaving the carbon–oxygen bond in Fischer–Tropsch hydrocarbon synthesis.

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‡ Calc. for UC$_{14}$H$_{18}$O$_2$: C, 36.8; H, 3.95; found: C, 35.4; H, 3.65%. The mass of the precipitate corresponded to that expected for a high yield of 'U(C$_5$H$_5$)$_2$O·thf.'

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