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FREE RADICAL SUBSTITUTION REACTIONS ON ZIRCONIUM AND HAFNIUM ORGANOMETALLICS

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Summary

Di-t-butyl nitroxide readily substitutes alkyl zirconocenes and hafnocenes, Cp_2MR_2, by a rate-determining displacement of alkyl radicals to give high yields of *O*-alkyl-*N*,*N*-di-t-butylhydroxylamine and $Cp_2M(R)ONBu^t_2$. A free radical substitution of di-benzylzirconocene by benzenethiyl radicals yields $Cp_2Zr(SPh)_2$.

Introduction

Free radical substitution reactions at the metal centre of organometallics have been reviewed by various authors [1] and the first reported example of such reactions in the case of transition metals was alkyl group displacement from square-planar platinum(II) complexes by thiyl radicals [2a]. We have reported examples of free radical autoxidations in solution of homoleptic early transition-metal alkyls of titanium, zirconium, molybdenum and tungsten [3], and more recently we have established that the mechanism in the case of alkyl zirconocenes and hafnocenes is a S_H2, free radical, chain reaction [4] involving alkylperoxy radicals. The rapid peroxydealkylation part of the propagation step was measured and the bimolecular rate constants for a number of compounds determined. We have also directed our efforts to finding further examples of S_H2 reactions at Group IVA organometallics having more moderate speeds which would be convenient for kinetic measurements. We now report attempts to bring about substitutions involving the di-t-butylnitroxide radical, benzenethiyl radical and alkoxy radicals.

Results and discussion

Di-t-butylnitroxide

The use of stable nitroxide free radicals to bring about homolytic substitu-

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tion at metal centres of organometallics has received little attention except for the case of bis(trifluoromethyl)nitroxide with tris(trifluoromethyl)arsenic [5]; the formation of *O*-norbornyl-*N*,*N*-di-t-butylhydroxylamine from the Grignard reagent and di-t-butyl nitroxide [6] also probably occurs via a S_H2 process.

We have found that two molecular equivalents of di-t-butylnitroxide, when added to a toluene solution of dibenzylzirconocene at ambient temperature, gives a smooth reaction to form the *O*-benzyl-*N*,*N*-di-t-butylhydroxylamine and a pale yellow substituted zirconocene:

$$Cp_2Zr(CH_2Ph)_2 + 2\ Bu^t_2NO^\cdot \rightarrow Cp_2Zr(CH_2Ph)ONBu^t_2 + Bu^t_2NOCH_2Ph \qquad (1)$$

The hydroxylamine was characterised by spectra comparisons with a sample prepared using benzyl Grignard and the nitroxide [6]. The pale yellow, somewhat air sensitive zirconocene has, we tentatively suggest (from a consideration of its IR spectrum), the oxygen bonded to the metal. We isolated the latter compound in 56% yield by low temperature crystallisation although ^1H NMR measurements indicated that the reaction was almost quantitative.

By observing the ^1H NMR line broadening effect of di-t-butylnitroxide on dioxane used as solvent, after the method of Evans [7], it was possible to establish a relative order of reactivity for a number of zirconocenes (Table 1). In order to establish that the S_H2 reaction occurred with displacement of a benzyl radical, the reaction was carried out in tetrahydrofuran in the presence of nitrosodurene, when the spin-trapped benzyl radical was observed in the ESR spectrum [8].

$$Bu^t_2NO^\cdot + Cp_2Zr(CH_2Ph)_2 \xrightarrow{k_d} Cp_2Zr(CH_2Ph)ONBu^t_2 + PhCH_2^\cdot \qquad (2)$$

This rate-determining step can be compared with similar displacements by alkylperoxy radicals [4] and alkoxy radicals. The slow step was followed by the well established alkyl radical-trapping reaction [9] to give the substituted hydroxylamine:

$$PhCH_2^\cdot + Bu^t_2NO^\cdot \xrightarrow{\text{fast}} PhCH_2ONBu^t_2 \qquad (3)$$

TABLE 1

BIMOLECULAR RATE CONSTANTS FOR FREE-RADICAL LIGAND SUBSTITUTION BY DI-t-BUTYL NITROXIDE [a]

Compound	k_d (35°C) (M^{-1} s^{-1})	Relative reactivity
$Hf(CH_2Ph)_4$	Too fast to measure	
$CpZr(CH_2Ph)_3$	Too fast to measure	
$Cp_2Zr(CH_2Ph)_2$	4.9×10^{-2}	1100
$Cp_2Zr(CH_2Ph)Br$	1.2×10^{-2}	520
$Cp_2Zr(CH_2Ph)Cl$	3.9×10^{-3}	170
$Cp_2Zr(CH_3)2$	8.3×10^{-4}	18
$(MeCp)_2Zr(CH_2Ph)_2$	1.1×10^{-4}	2.4
$Cp_2Hf(CH_2Ph)_2$	4.6×10^{-5}	1.0
$Cp_2Zr(CH_3)Cl$	Too slow for accurate measurement	

[a] The relative reactivities in Table 1 are statistically corrected to take into account the numbers of displaceable alkyl groups.

The asymmetric (methyl)benzylzirconocene, $Cp_2Zr(CH_3)CH_2Ph$, gave only *O*-benzyl-*N*,*N*-di-t-butylhydroxylamine and $Cp_2Zr(CH_3)ONBu^t_2$; dibenzylzirconocene was significantly more reactive than the dimethylzirconocene (Table 1) in agreement with the ease of displacement of the resonance-stabilised benzyl radical. Further evidence for a S_H2 displacement of alkyl radicals was observed when a low concentration of the nitroxide was added to the significantly more reactive tetrabenzylhafnium; there was a rapid depletion of nitroxide so that termination by alkyl radical coupling became significant and ca. 40% of the benzyl radicals resulted in dibenzyl formation.

Additional evidence for the mechanism resulted for the NMR line broadening measurements. Application of the steady-state approximation to eqs. 2 and 3 gave on integration an equation of the form:

$$\ln[a(b-2x)/b(a-x)] = (b-2a)\,k_d t \qquad (4)$$

where a and b are the initial concentrations of organometallic and nitroxide, respectively and x = organometallic consumed in time t. Plots of eq. 4 for the organometallics in Table 1 gave straight line graphs (Fig. 1), the slopes of which gave the bimolecular rate constants k_d at 35°C.

Both tetrabenzylhafnium and monocyclopentadienylzirconiumtribenzyl were too reactive for k_d to be measured, due to the increased number of vacant orbitals (five vacant orbitals in the former, three in the latter) providing greater ease of access to the attacking radical. On the other hand, $Cp_2Zr(CH_3)Cl$ was too slow to measure accurately, partly as a result of π back bonding from the chlorine to the one vacant orbital on the zirconium, and partly due to inductive destabilisation by electronegative chlorine of the dipolar contribution to the activated complex in eq. 2, reducing the ease of free radical displacement. A

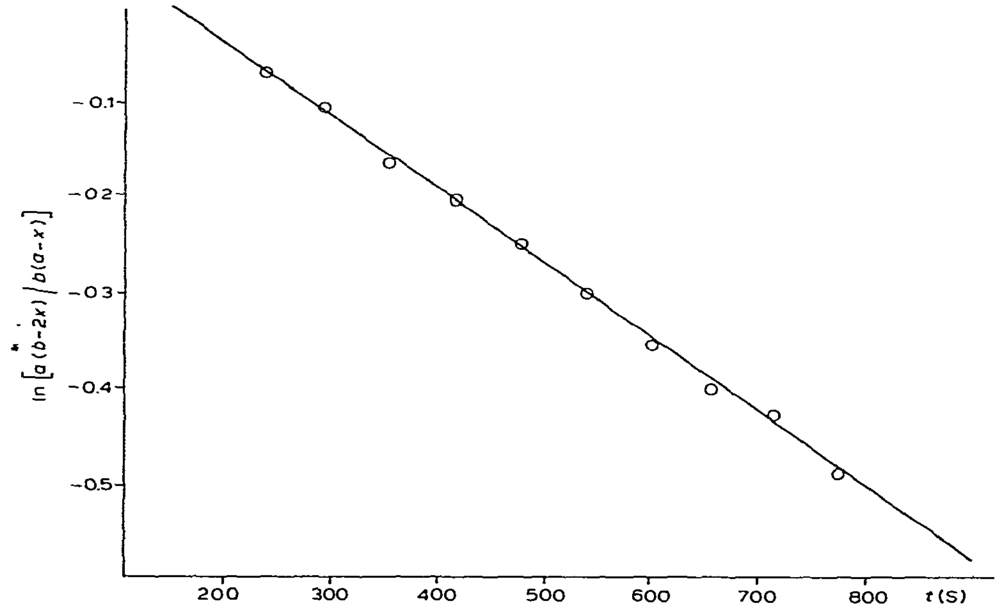

Fig. 1. Interaction of benzylzirconocene chloride and di-t-butylnitroxide at 35°C.

similar effect had been noticed between dioxygen and halogen-substituted zirconocenes [4]. When methyl-substituted cyclopentadienyl ligands were incorporated in the zirconocene a steric retardation was observed. This is in keeping with the observation that there was increased non-equivalence of the cyclopentadienyl protons in $(CH_3Cp)_2Zr(CH_2Ph)ONBu^t_2$ (as demonstrated by 90 MHz, ^{1}H NMR) compared with the starting compound.

Benzenethiol

Chain reactions involving alkylthiol radicals and metal alkyls have been demonstrated [2] using either the thiol or the disulphide. When we added benzenethiol to dibenzylzirconocene in carefully degassed solutions, the yellow crystalline dithiolate was formed in 77% yield,

$$Cp_2Zr(CH_2Ph)_2 + 2\ PhSH \rightarrow Cp_2Zr(SPh)_2 + 2\ PhCH_3 \qquad (5)$$

The technique of significantly altering the overall rate of a free radical chain reaction by adding small amounts of radical initiators or free radical inhibitors is well established. We therefore repeated the experiment in the presence of 5 mol% of di-t-butylhyponitrite, which caused a 50% increase in the extent of reaction over a one hour period. The effect was not observed when diphenyldisulphide was substituted for the thiol. When reaction 5 was carried out in the presence of galvinoxyl inhibitor no change in rate was observed. It would seem that there is a non-free radical route to the dithiolate, involving replacement of the thiol's acidic hydrogen similar to the previously reported reaction with hydroperoxide or alcoholysis with benzyl alcohol [4]. Self initiation by extraneous zirconocene peroxide is unlikely, since we have demonstrated that these peroxides rapidly rearrange to the alkoxide [4]. The initiated thiol reaction is represented by eqs. 6 to 9.

$$Bu^tON{=}NOBu^t \rightarrow 2\ Bu^tO^{\cdot} + N_2 \qquad (6)$$

$$Bu^tO^{\cdot} + PhSH \rightarrow Bu^tOH + PhS^{\cdot}$$

$$PhS^{\cdot} + Cp_2ZrR_2 \rightarrow Cp_2Zr(R)SPh + R^{\cdot} \qquad (7)$$

$$R^{\cdot} + PhSH \rightarrow RH + PhS^{\cdot} \qquad (8)$$

$$PhS^{\cdot} + Cp_2Zr(R)SPh \rightarrow Cp_2Zr(SPh)_2 + R^{\cdot} \qquad (9)$$

Alkoxyradical reactions

It has been shown that the autoxidation of zirconocenes can be initiated by butoxy radicals derived from di-t-butylhyponitrite [4] because the butoxy radicals served to abstract hydrogen from the toluene solvent to give increased numbers of chain-propagating benzyl radicals. Photolytically generated t-butoxy radicals have been shown by ESR spectroscopy to give S_H2 reactions at the metal centres of dialkylzirconocenes [9]. H.C. Brown et al. [10] discovered that α,β-unsaturated aldehydes undergo (S_H2-initiated) free-radical 1,4-addition with trialkylboranes; the chain-carrying species are oxygen-centred radicals with conjugative stabilisation. In order to see if a similar 1,4-addition would occur at zirconium, tetrabenzylzirconium and acrolein were interacted. However, 1,2-

addition produced 3-hydroxy-4-phenylbut-1-ene after hydrolysis;

$$CH_2{=}CHCHO + R{-}ZrR_3 \rightarrow CH_2{=}CHCH(R)OZrR_3 \xrightarrow{H_2O} CH_2{=}CHCH(R)OH + 3\ RH + ZrO_2 \cdot n\ H_2O \quad (10)$$

and in this respect the zirconium alkyl resembled the Grignard-acrolein reaction [11].

Experimental

All experiments were carried out under dry, oxygen-free conditions.

Interaction of zirconocenes and di-t-butylnitroxide

Di-t-butylnitroxide (1.6 g, 11 mmol) was added dropwise to a stirred toluene solution (27 cm^3) of dibenzylzirconocene (2.2 g, 5.5 mmol) at 20°C, and stirring was continued for 3 h, during which time the colour changed from orange to yellow. Hexane (30 cm^3) was added and the mixture cooled to —72°C. Pale yellow crystals of benzylzirconocene di-t-butylnitroxide, $Cp_2Zr(CH_2Ph)ONBu^t_2$, were separated and washed with hexane and dried under vacuum (1.4 g, 56%). (Found: C, 66.1; H, 7.9; N, 3.1. $C_{25}H_{35}ONZr$ req.: C, 65.7; H, 7.7; N, 3.1%). The IR bands at 525 and 435 cm^{-1} correspond to Zr—C and Zr—O [11] stretching vibrations (cf. $Cp_2Zr(CH_2Ph)OCH_2Ph$ bands at 535 and 455 cm^{-1}). The isolation of pure *O*-benzyl-*N*,*N*-di-t-butylhydroxylamine, free of solvent, was not pursued; rather it was identified by comparison of its IR, mass and ^{1}H NMR spectra with an authentic sample prepared from benzyl Grignard and the nitroxide [6], which after filtration and aqueous treatment yielded the hydroxylamine derivative.

$$PhCH_2MgCl + 2\ Bu^t_2NO^{\cdot} \xrightarrow{\text{ether}} Mg(ONBu^t_2)\ Cl + PhCH_2ONBu^t_2 \quad (11)$$

There was a strong C—O IR stretch at 1025—1050 cm^{-1} but no amine oxide band at 950—970 cm^{-1} in both samples. The mass spectra both had molecular

TABLE 2

^{1}H NMR DATA FOR COMPOUNDS WITH NITROXIDE LIGANDS IN C_6D_6 SOLVENT (τ)

Compound	Cp	CH_2	Me	Bu^t
$Cp_2Zr(CH_2C_6H_4CH_3\text{-}o)ONBu^t_2$	4.15	7.69	7.69	8.83
$Cp_2Zr(CH_2C_6H_4CH_3\text{-}m)ONBu^t_2$	4.13	7.52	7.68	8.84
$Cp_2Zr(CH_2C_6H_4CH_3\text{-}p)ONBu^t_2$	4.11	7.49	7.70	8.83
$Cp_2Zr(CH_2C_6H_4Cl\text{-}m)ONBu^t_2$	4.21	7.64	—	8.87
$Cp_2Zr(CH_2C_6H_4Cl\text{-}p)ONBu^t_2$	4.20	7.66	—	8.88
$Cp_2Zr(CH_2C_6H_4F\text{-}p)ONBu^t_2$	4.18	7.64	—	8.87
$Cp_2Zr(CH_2C_{10}H_7\text{-}1)ONBu^t_2$	4.16	7.11	—	8.80
$Cp_2Zr(CH_2C_{10}H_7\text{-}2)ONBu^t_2$	4.16	7.36	—	8.83
$(MeCp)_2Zr(CH_2Ph)ONBu^t_2$	3.9 —4.4(m)	7.53	8.04	8.81
$Cp_2Zr(Cl)ONBu^t_2$	3.90	—	—	8.83
$Cp_2Zr(Br)ONBu^t_2$	3.89	—	—	8.83
$Cp_2Zr(CH_3)ONBu^t_2$	4.13	—	9.65	8.88
$Cp_2Hf(CH_2Ph)ONBu^t_2$	4.17	7.71	—	8.85
$Cp_2Zr(CH_2Ph)ONBu^t_2$	4.13	7.48	—	8.85

ions m/e = 235. The ^{1}H NMR spectra in benzene-d_6 (90 MHz) showed multiplet at τ 2.6—3.0 (C_6H_5); singlet 5.14 (CH_2) and singlet 8.72 (CH_3). The nitroxide derivative from di(methylcyclopentadienyl)zirconium dibenzyl had a much more complex ^{1}H NMR cyclopentadienyl proton absorption (Table 2) compared to the starting compound [4] τ 4.53.

Kinetic measurements

A benzene-d_6 solution of the organometallic (0.5 cm^3, 0.2 M) together with purified 1,4-dioxane (0.2 M) under nitrogen was placed in an NMR sample tube sealed with a serum cap. Di-t-butyl nitroxide solution (0.10 mmol) was injected, with mixing, into the tube and the 90 MHz, ^{1}H NMR spectrum at 35°C examined. The height of the 1,4-dioxane absorption increased with time in relationship to the nitroxide concentration [7]. Using a previously prepared calibration curve the nitroxide concentration was determined. Instrument stability was checked by recording the calibration spectra immediately before and after each experiment. Experiment times varied from a few minutes for dibenzylzirconocene to six hours for dibenzylhafnocene. Using the latter it was possible to check that the metallocene did not affect the line broadening property of the nitroxide. The compounds listed in Table 1 were prepared as described elsewhere [4] and the relative reactivities obtained using eq. 4.

Tetrabenzylhafnium and di-t-butylnitroxide

This reaction was too rapid at 35°C to follow by the above method; however, when di-t-butyl nitroxide (0.14 g, 1.0 mmol) in benzene-d_6 (0.5 cm^3) was added dropwise to a stirred solution of tetrabenzylhafnium (0.5 g, 1.0 mmol) in benzene-d_6 (5 cm^3), *O*-benzyl-*N*,*N*-di-t-butylhydroxylamine and dibenzyl were found to be present in the mol ratio 3.2 : 1. The reaction mixture was shielded from light and the temperature kept below 20°C to eliminate photolysis or thermolysis effects. After hydrolysis the ratio was unchanged; the compounds were confirmed by ^{1}H NMR and GLC retention time.

Interaction of zirconocenes with C-nitroso compounds

With a view to establishing eq. 2, spin-trapping experiments were considered and nitrosodurene was found to be suitable. Other nitroso compounds and nitrones reacted with the organometallic. When di-t-butylnitroxide (1 mol eq.)

TABLE 3

^{1}H NMR DATA FOR *O*-ALKYL-*N*,*N*-DI-*t*-BUTYLHYDROXYLAMINES (τ)

Compound	CH_2	Me	Bu^t
$Bu^t_2NOCH_2C_6H_4CH_3$-*o*	5.13	7.85	8.72
$Bu^t_2NOCH_2C_6H_4CH_3$-*m*	5.14	7.86	8.70
$Bu^t_2NOCH_2C_6H_4CH_3$-*p*	5.13	7.86	8.69
$Bu^t_2NOCH_2C_6H_4Cl$-*m*	5.31	—	8.76
$Bu^t_2NOCH_2C_6H_4Cl$-*p*	5.33	—8.6	8.76
$Bu^t_2NOCH_2C_6H_4F$-*p*	5.30	—	8.74
$Bu^t_2NOCH_2C_{10}H_7$-1	4.64	—	8.68
$Bu^t_2NOCH_2C_{10}H_7$-2	5.00	—	8.68
$Bu^t_2NOCH_3$	—	6.49	8.77

was added to dibenzylzirconocene (25 mol eq.) 0.075 *M* in tetrahydrofuran, together with nitrosodurene (2.5 mol eq.) the ESR spectrum of the trapped benzyl radical, superimposed on the nitroxide spectrum, was observed [8]. The spectrum faded over 15 minutes.

Interaction of dibenzylzirconocene and benzenethiol

Benzenethiol (1.4 g, 13 mmol) and di-t-butyl hyponitrite (0.05 g, 0.3 mmol) were added to dibenzylzirconocene (2.3 g, 5.8 mmol) in benzene (29 cm^3), and stirring was continued for 3 h at 45°C. The solvent was removed under vacuum and the crude product recrystallised from toluene (30 cm^3) by addition of hexane (30 cm^3) and cooling to —72°C when the yellow dithiolate (2.0 g, 77%) crystallised. ^{1}H NMR: singlet τ 4.35 (Cp), multiplet 2.0—2.3 (C_6H_5). The IR spectrum agreed with published data [11,12]. When the reaction was repeated at 50°C in the NMR tube using gas-tight syringes and serum caps the rate of reaction could be followed from the toluene absorption at τ 7.85 over 1 hour. Galvinoxyl (10 mol%) had no effect on the reaction. When di-t-butyl hyponitrite (5 mol%) was added there was a ca. 50% increase in intensity of the toluene absorption. The absence of any absorption at τ 7.62 [4] eliminates $Cp_2Zr(CH_2Ph)OBu^t$ as an intermediate in the reaction.

Interaction of tetrabenzylzirconium and acrolein

Freshly distilled acrolein (1.1 g, 20 mmol) was added dropwise to a vigorously stirred solution of tetrabenzylzirconium (4.6 g, 10 mmol) in ether at 0°C. After 45 minutes the solvent was removed under vacuum and found to be free of any acrolein. The off-white residue, after aqueous treatment and extraction with benzene, gave 3-hydroxy-4-phenyl-but-1-ene (80%) which was identified by comparison of its IR spectrum with a sample prepared using the Grignard reagent [13]. There was no evidence of any C=O stretching absorption. The mass spectrum had a molecular ion *m/e* = 148.

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