

Reactions of the triosmium cluster $\text{Os}_3(\mu\text{-H})(\mu\text{-OH})(\text{CO})_{10}$ with naphthols

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Abstract

Reaction of the cluster $\text{Os}_3(\mu\text{-H})(\mu\text{-OH})(\text{CO})_{10}$ (**1**) with 1-naphthol afforded the isomeric clusters **2a** and **3a** with the formulae $\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-1-OC}_{10}\text{H}_6)(\text{CO})_9$. A similar reaction with 2-naphthol, however, gave $\text{Os}_3(\mu\text{-H})(\mu\text{-2-OC}_{10}\text{H}_7)(\text{CO})_{10}$, **4b**, and the analogue of **2a**. These clusters have been structurally characterised to confirm the mode of anchoring of the naphthols.
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1. Introduction

We have been interested in whether cluster-bound substrates may be gainfully employed in organic transformations [1]. An interesting class of substrates are the aromatics. For instance, in a series of papers, Rosenberg and coworkers have demonstrated that the anchoring of quinolines onto triosmium clusters can be utilised in modifying the stereochemistry of reactions at the quinolines [2]. Similarly, cluster-bound phenylenes can undergo not only the expected Friedel–Crafts reactions [3] but also carbonylation [4]. A related aromatic system that we were interested in was the naphthols; we wanted to find out if we may be able to induce reactions at the cluster-bound naphthols. The reaction of the naphthols with $\text{Os}_3(\text{CO})_{12}$ has previously been studied by Deeming and coworkers [5]. They had found that 2-naphthol reacted at 140 °C to afford a decacarbonyl and a nonacarbonyl cluster. On the other hand, 1-naphthol gave only the nonacarbonyl derivative; the decacarbonyl derivative that was normally obtained from similar reactions with simple alcohols [1,6], was not observed (Scheme 1). It was proposed that some of these species (e.g. 1-naphthol) were able to convert to the nonacarbonyl

bonyl $\text{Os}_3(\mu\text{-H})_2(\mu\text{-OR})(\text{CO})_9$ without forming the decacarbonyl $\text{Os}_3(\mu\text{-H})(\mu\text{-OR})(\text{CO})_{10}$, whereas in others (e.g. 2-naphthol), this conversion to the nonacarbonyl species via further loss of CO and C–H activation only occurred at higher temperatures.

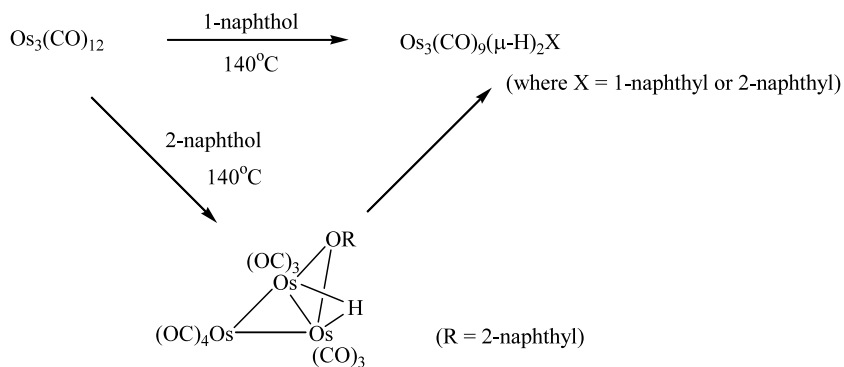
In our study, we sought an alternative route to these clusters. It has been reported that alkoxy-bridged triosmium clusters can be conveniently prepared from the cluster $\text{Os}_3(\mu\text{-H})(\mu\text{-OH})(\text{CO})_{10}$ (**1**) under mild conditions [7], and we have earlier successfully employed the methodology to anchor diols onto a triosmium cluster [1]. We were therefore interested in investigating whether we may be able to access the decacarbonyl derivative of 1-naphthol via this route. More importantly, we wanted to confirm the structures of the cluster-bound naphthol products, which were originally proposed on the basis of spectroscopic data. Our attempt is reported here.

2. Results and discussion

The principal products obtained from the reaction of **1** with the naphthols were essentially the same as those obtained earlier and are summarised in Scheme 2 below [5]. With 1-naphthol, two isomers **2a** and **3a** with the formulation $\text{Os}_3(\mu\text{-H})_2(\mu\text{-1-O-C}_{10}\text{H}_6)(\text{CO})_9$ and bearing a triply bridging 1-naphthyl moiety, were obtained.

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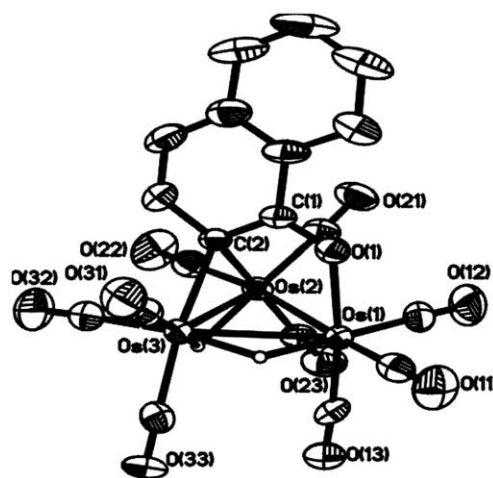
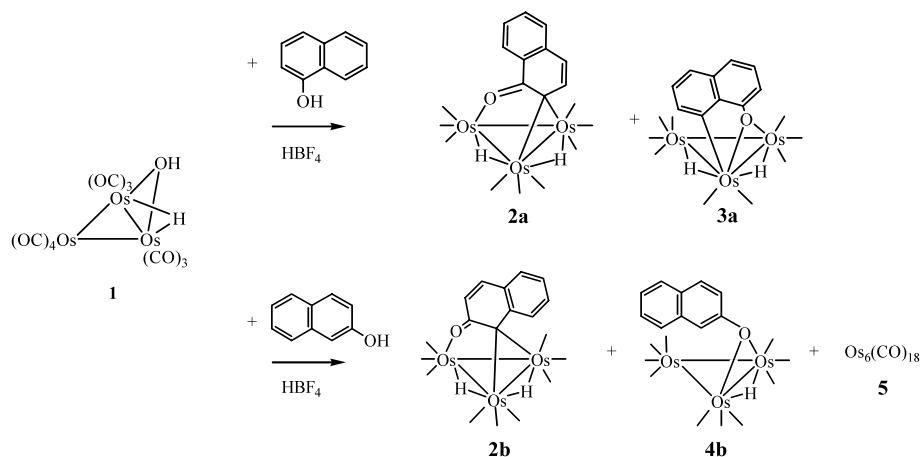
E-mail address: chmlwk@nus.edu.sg (W.K. Leong).



Scheme 1.

With 2-naphthol, a decacarbonyl cluster $\text{Os}_3(\mu\text{-H})(\mu\text{-}2\text{-O-C}_{10}\text{H}_7)(\text{CO})_{10}$ (**4b**) and a nonacarbonyl cluster $\text{Os}_3(\mu\text{-H})_2(\mu\text{-}2\text{-O-C}_{10}\text{H}_6)(\text{CO})_9$ (**2b**) with a triply bridging 2-naphthyl ligand, were obtained. The addition of tetrafluoroboric acid was essential to obtain full conversion of **1** to the respective naphthyl products. The product distribution could also be controlled through the temperature of the reaction. Thus the use of ambient temperature in the reaction with 2-naphthol allowed the isolation of **4b** as the only product. Thermolysis of **4b** in refluxing toluene afforded **2b** and **5**, confirming that **4b** is the initial reaction product. Similarly, **3a** was formed as the major product in about 85% yield by lowering the reaction temperature with 1-naphthol to 40 °C; no intermediate decacarbonyl of the type $\text{Os}_3(\mu\text{-H})(\mu\text{-OR})(\text{CO})_{10}$ was observed even under such mild conditions, however. Furthermore, thermolysis of **3a** in refluxing toluene afforded **2a**. In contrast, **2a** was stable at refluxing toluene temperature but gave initially a species (which does not survive TLC separation) with a hydride signal at -20.69 ppm on heating in the presence of HBF_4 ; **3a** was not formed. These observations suggest that **2a** is the irreversible isomerisation product from **3a** at elevated temperatures.

The structures of **2a**, **2b**, **3a** and **4b**, have been confirmed by single crystal X-ray crystallographic studies (Figs. 1–4, respectively); selected bond parameters for these clusters are given in Fig. 5. The bonding in **4b** is similar to that of other known alkoxy-bridged clusters [1,6]. As may therefore be anticipated, the C–C bond distances within the naphthyl ring show variations

Fig. 1. ORTEP diagram (organic hydrogens omitted, 50% probability thermal ellipsoids) for **2a**.

Scheme 2.

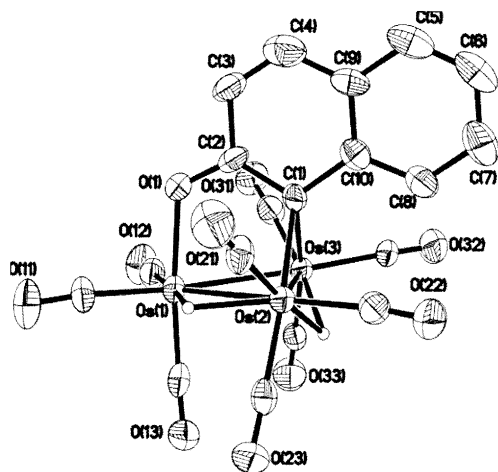


Fig. 2. ORTEP diagram (organic hydrogens omitted, 50% probability thermal ellipsoids) for **2b**.

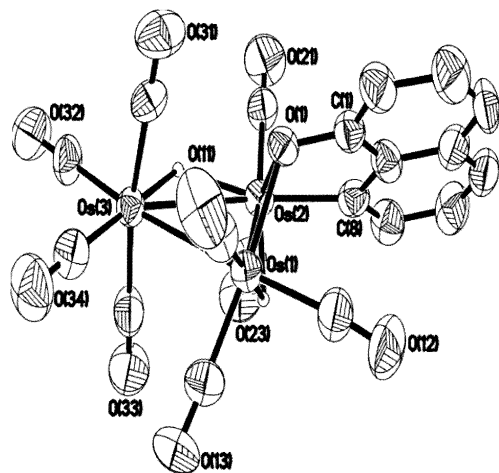


Fig. 3. ORTEP diagram (organic hydrogens omitted, 50% probability thermal ellipsoids) for **3a**.

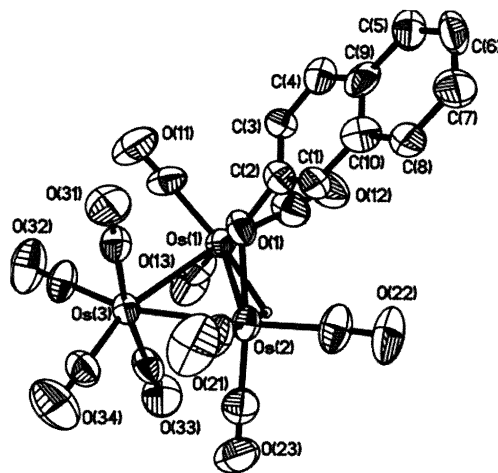


Fig. 4. ORTEP diagram (organic hydrogens omitted, 50% probability thermal ellipsoids) for **4b**.

consistent with that of free naphthalene (the C(1)–C(2) and C(2)–C(3) distances in naphthalene are 1.36 and 1.415 Å, respectively) [8]. The aromaticity of the naphthyl ring is thus retained upon coordination to the cluster.

Clusters **2a**, **2b** and **3a** contain a metallated OC_{10}H_6 ligand, but while it is the oxygen atom which is bridging two osmium atoms in **3a**, it is a carbon atom of the naphthyl ring that is bridging across two osmium atoms in **2**. The naphthyl rings in **2a** and **2b** are better described as rather non-aromatic and ketonic in nature, as depicted in Fig. 5. This has already been observed in closely related clusters such as $\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-OC}_6\text{H}_3\text{CH}_2\text{Ph})(\text{CO})_9$ [9], and the bond parameters are in line with this description. Thus the C–O bond lengths (1.294 (12) and 1.304(11) Å for **2a** and **2b**, respectively) are found to be intermediate between those for C–O single and C=O double bonds (~ 1.34 Å and 1.21 Å, respectively) [8], while the C(1)–C(2) bond distances (1.427(12) and 1.447(13) Å for **2a** and **2b**, respectively) are considerably longer than the partial C–C and C=C bond distances in the aromatic naphthalene ring (1.36 and 1.415 Å respectively) [8b].

Thus we have shown that naphthols can be anchored onto triosmium via cluster **1** in a very selective manner by control of the reaction conditions employed. The next step is to explore the reactivity of these naphthyl derivatives with organic substrates.

3. Experimental

All reactions and manipulations were carried out under nitrogen by using standard Schlenk techniques. NMR spectra were recorded at ambient temperature on a Bruker ACF-300 FT-NMR spectrometer in CDCl_3 unless otherwise stated. IR spectra were recorded as hexane solutions, unless otherwise stated. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. All reagents were from commercial sources and used as supplied. The cluster $\text{Os}_3(\mu\text{-H})(\mu\text{-OH})(\text{CO})_{10}$ (**1**) was prepared according to the literature method [7].

3.1. Reaction of **1** with 1-naphthol

A solution of **1** (63.9 mg, 73.6 μmol) in toluene (60 ml), 1-naphthol (173.0 mg, 1.20 mmol) and aqueous HBF_4 (seven drops) was refluxed under nitrogen for 6 h in a 100 ml, three-necked, round-bottomed flask. The brown solution obtained was evaporated to dryness and the residue was subjected to TLC separation with CH_2Cl_2 –hexane (1:1, v/v) as eluant to afford, besides unreacted **1** (6.3 mg), yellow crystalline $\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-1-OC}_{10}\text{H}_6)(\text{CO})_9$ (**2a**) ($R_f = 0.74$, 5.6 mg, 8%) and orange

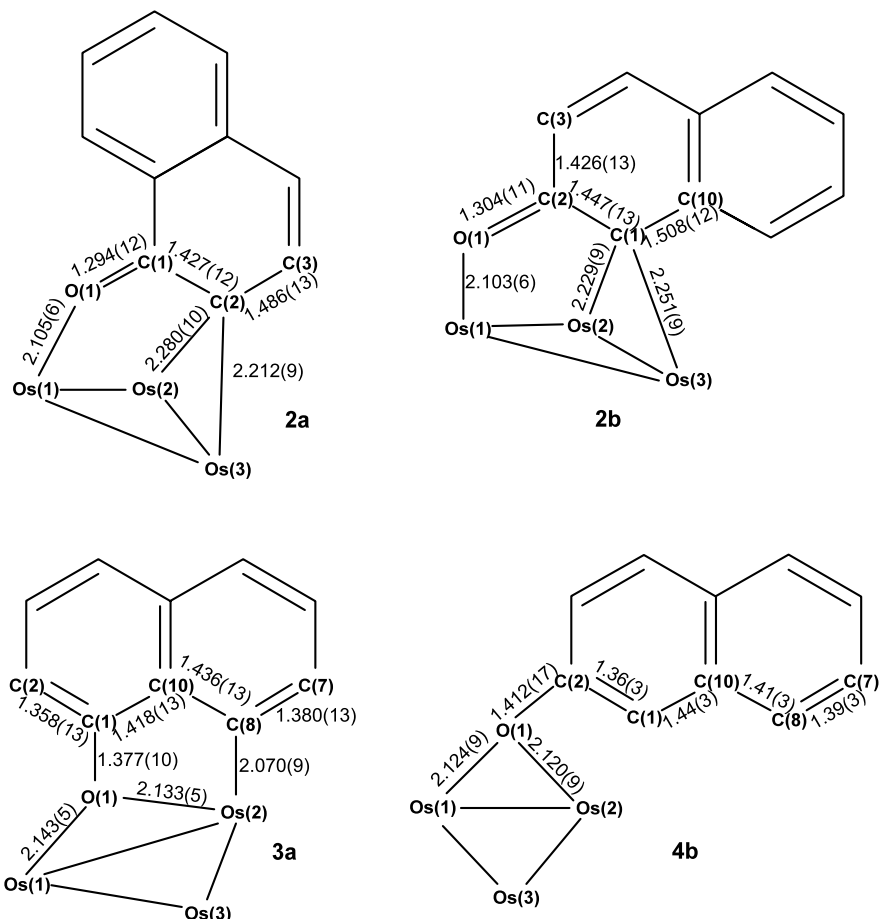


Fig. 5. Selected bond parameters for **2a**, **2b**, **3a** and **4b**.

$\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-1-OC}_{10}\text{H}_6)(\text{CO})_9$ (**3a**) ($R_f = 0.68$, 49.3 mg, 69%).

2a: $\nu_{\text{CO}}/\text{cm}^{-1}$: 2108w, 2084s, 2055vs, 2031m, 2026m, 2013m, 2001s, 1980w (lit.(cyclohexane) [5]: 2108m, 2083vs, 2055vs, 2032m, 2025m, 2012m, 1998s, 1980m); $^1\text{H-NMR}$ δ 8.16 (m, 1H, naphthyl), 7.76 (m, 1H, naphthyl), 7.46 (m, 1H, naphthyl), 6.86 (d, 1H, H(3) or H(4)), $^3J_{\text{HH}} = 8.2$ Hz), 6.27 (d, 1H, H(3) or H(4)), –11.54 (d, 1H, OsHOs, $^2J_{\text{HH}} = 1.5$ Hz), –13.80 (d, 1H, OsHOs).

3a: $\nu_{\text{CO}}/\text{cm}^{-1}$: 2129w, 2085s, 2054vs, 2049vs, 2042vs, 2031m, 2016m, 2000m, 1972s (lit.(cyclohexane) [5]: 2126m, 2085vs, 2054vs, 2048vs, 2042vs, 2030m, 2015m, 1998m, 1972m); $^1\text{H-NMR}$ δ 7.88 (dd, 1H, naphthyl, $^3J_{\text{HH}} = 7.5, 2.0$ Hz), 7.5–7.0 (m, 4H, naphthyl), 6.84 (dd, 1H, naphthyl, $^3J_{\text{HH}} = 3.3, 7.5$ Hz), –11.05 (s, 1H, OsHOs), –14.83 (s, 1H, OsHOs).

3.2. Reaction of **1** with 2-naphthol

A similar reaction as above between **1** (241.8 mg, 279 μmol) and 2-naphthol (67.1 mg, 466 μmol) gave three major products, viz., yellow $\text{Os}_3(\mu\text{-H})(\mu\text{-2-OC}_{10}\text{H}_7)(\text{CO})_{10}$, **4b** ($R_f = 0.78$, 37.1 mg, 15%), orange

crystalline $\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-2-OC}_{10}\text{H}_6)(\text{CO})_9$, **2b** ($R_f = 0.46$, 2.7 mg, 1%), and dark brown $\text{Os}_6(\text{CO})_{18}$, **5** ($R_f = 0.27$, 1.0 mg, 4%).

2b: $\nu_{\text{CO}}/\text{cm}^{-1}$: 2107w, 2083vs, 2054vs, 2032s, 2021m, 2012m, 2001s, 1978w (lit.(cyclohexane) [5]: 2108m, 2083vs, 2055vs, 2032s, 2022m, 2013m, 2002s, 1988w, 1980m); $^1\text{H-NMR}$ δ 8.06 (d, 1H, naphthyl, $^3J_{\text{HH}} = 9.5$ Hz), 7.42 (m, 4H, naphthyl), 6.48 (d, 1H, naphthyl), –10.70 (d, 1H, OsHOs, $^2J_{\text{HH}} = 1.5$ Hz), –13.35 (d, 1H, OsHOs).

4b: $\nu_{\text{CO}}/\text{cm}^{-1}$: 2112w, 2073vs, 2064s, 2025vs, 2007s, 1991m, 1987m (lit.(cyclohexane) [5]: 2112m, 2073vs, 2064s, 2037m, 2025vs, 2007s, 1991m, 1987m); $^1\text{H-NMR}$ δ 7.8–7.1 ppm (m, 5H, naphthyl), 6.73 (m, 2H, naphthyl), –11.97 (s, 1H, OsHOs).

5: $\nu_{\text{CO}}/\text{cm}^{-1}$: 2112w, 2086vs, 2058vs, 2038m, 2031m, 2027m, 2014m, 2004s, 1979w. Crystal data: $a = 18.8506(1)$ Å, $b = 17.9166(2)$ Å, $c = 17.8994(2)$ Å, $\beta = 113.110(1)^\circ$, monoclinic, space group $P2_1/c$.

3.3. Thermolysis of **3a**

A solution of **3a** (49.3 mg, 51 μmol) in toluene (25 ml) and HBF_4 in ether (eight drops) was refluxed under

Table 1
Crystal data for **2a**, **2b**, **3a** and **4b**

Compound	2a	2b	3a	4b
Empirical formula	C ₁₉ H ₈ O ₁₀ Os ₃	C ₁₉ H ₈ O ₁₀ Os ₃	C ₁₉ H ₈ O ₁₀ Os ₃	C ₂₀ H ₈ O ₁₁ Os ₃
Formula weight	966.85	966.85	966.85	994.86
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	8.9835(2)	15.8406(4)	9.5230(2)	8.7762(1)
<i>b</i> (Å)	9.0531(2)	8.7298(2)	12.9880(1)	29.9606(3)
<i>c</i> (Å)	16.2080(4)	16.4580(4)	18.1819(2)	9.2485(1)
α (°)	92.459(1)	90	90	90
β (°)	101.562(1)	111.925(1)	90	97.260(1)
γ (°)	118.128(1)	90	90	90
<i>V</i> (Å ³)	1124.41(4)	2111.29(9)	2248.82(6)	2412.31(4)
Number of reflections to determine cell parameters	6644	8192	5755	8192
<i>Z</i>	2	4	4	4
<i>D</i> _{calc} (g cm ⁻³)	2.856	3.042	2.856	2.739
Absorption coefficient (mm ⁻¹)	16.960	18.064	16.960	15.818
<i>F</i> (000)	860	1720	1720	1776
Crystal size (mm)	0.46 × 0.31 × 0.06	0.24 × 0.22 × 0.08	0.40 × 0.38 × 0.34	0.28 × 0.28 × 0.26
Theta range for data collection (°)	2.58–29.17	1.52–29.28	2.24–29.22	2.32–29.24
Reflections collected	8359	16 021	14 772	19 394
Independent reflections	5215 [<i>R</i> _{int} = 0.0291]	5238 [<i>R</i> _{int} = 0.0565]	5609 [<i>R</i> _{int} = 0.0255]	5976 [<i>R</i> _{int} = 0.0525]
Max. and min. transmission	0.154 and 0.010	0.297 and 0.106	0.049 and 0.018	0.090 and 0.037
Data/restraints/parameters	5215/2/292	5238/0/289	5609/1/292	5976/26/341
Goodness-of-fit on <i>F</i> ²	1.047	0.990	1.223	1.262
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0429, <i>wR</i> ₂ = 0.1220	<i>R</i> ₁ = 0.0393, <i>wR</i> ₂ = 0.0943	<i>R</i> ₁ = 0.0284, <i>wR</i> ₂ = 0.0689	<i>R</i> ₁ = 0.0535, <i>wR</i> ₂ = 0.1136
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0490, <i>wR</i> ₂ = 0.1277	<i>R</i> ₁ = 0.0593, <i>wR</i> ₂ = 0.1026	<i>R</i> ₁ = 0.0317, <i>wR</i> ₂ = 0.0713	<i>R</i> ₁ = 0.0705, <i>wR</i> ₂ = 0.1231
Largest difference peak and hole (e Å ⁻³)	2.162 and -3.141	1.885 and -3.602	0.671 and -1.574	1.537 and -1.897
Absolute structure parameter	–	–	0.011(18)	–

nitrogen for 6 h. The light brown solution so obtained was evaporated to dryness and the residue subjected to TLC separation with CH₂Cl₂–hexane (1:1, v/v) as eluant. The two major bands obtained were identified spectroscopically as **2a** (12.3 mg, 25%) and unreacted **3a** (20.3 mg, 41%).

3.4. Thermolysis of **4b**

A solution of **4b** (127.1 mg, 127 μmol) in toluene (25 ml) and HBF₄ in ether (eight drops) was refluxed under nitrogen for 6 h. The light brown solution so obtained was treated as above to afford unreacted **4b** (29.8 mg, 15%), **2b** (27.0 mg, 10%) and **5** (1.4 mg, 4%).

3.5. Crystal structure determinations

Crystals were grown by slow cooling from CH₂Cl₂/hexane solutions and mounted on quartz fibres. X-ray data were collected on a Bruker AXS APEX system, using Mo–K α radiation, with the SMART suite of programs [10]. Data were corrected for Lorentz and

polarisation effects with SAINT [11], and for absorption effects with SADABS [12]. The final unit cell parameters were obtained by least squares on a number of strong reflections. Structural solution and refinement were carried out with the SHELXTL suite of programs [13]. Crystal and refinement data are summarised in Table 1.

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Organic H atoms were generally placed in calculated positions and given isotropic thermal parameters at 1.5 times that of the C atoms to which they are attached. The metal hydride positions were either located by low angle difference maps (**4b**) and their positions refined but with the isotropic thermal parameters fixed, or were placed in calculated positions with XHYDEX (**2a**, **2b** and **3a**) [14]. All non-hydrogen atoms were given anisotropic thermal parameters in the final models.

The naphthyl ring in **4b** was disordered; this was modelled with two alternative conformations, with appropriate restraints on the carbon atom positions and thermal parameters.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 177433–177436. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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