Surface-supported Group 5 Metal Organometallic Compounds for Catalytic Arene Hydrogenation

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The Group 5 metal alkylidyne bridged compounds $[(Me_3SiCH_2)_2M(\mu\text{-}CSiMe_3)_2M(CH_2SiMe_3)_2]$ (M = Nb, Ta) supported on silica will catalyse the exhaustive hydrogenation of a variety of aromatic substrates.

The area of heterogeneous catalytic hydrogenation of aromatic compounds has historically been dominated by the use of the platinum group metals as catalysts.[1] Recent research in our group has shown that the homogeneous hydrogenation of aromatic substrates is possible using Group 5 metal hydride compounds containing ancillary oxygen donor (aryl oxide) ligation.[2] As an extension of this work we report here our observations concerning the high catalytic activity of silica-supported niobium and tantalum organometallic compounds for carrying out heterogeneous arene hydrogenation.

The chemistry of early d-block metal organometallic compounds attached to metal oxide supports has an extensive history,[3] particularly with regard to their activity towards alkene substrates. We find that a variety of Group 4 and Group 5 metal alkyl compounds supported on silica will catalyse the hydrogenation of benzene to cyclohexane and

Table 1 Hydrogenation of benzene and naphthalene by silica-supported d-block organometallic compounds

Compound	Benzene[a]			Naphthalene[b]		
	Benzene[c]	Cyclohexane[c]	*t*/min	*trans*-Decalin[c]	*cis*-Decalin[c]	*t*/min
$[Ti(CH_2SiMe_3)_4]$	61	39	360	45	55	150[d]
$[Zr(CH_2Ph)_4]$	0	100	240[d]	75	25	30[d]
$[Hf(CH_2Ph)_4]$	0	100	600[d]	81	19	60[d]
$[\{Nb(\mu\text{-}CSiMe_3)(CH_2SiMe_3)_2\}_2]$ **1a**	0	100	300[d]	48	52	20[d]
$[\{Ta(\mu\text{-}CSiMe_3)(CH_2SiMe_3)_2\}_2]$ **1b**	0	100	720[d]	85	15	70[d]
$[Ta(CH_2C_6H_4\text{-}Me\text{-}4)_5]$	68	32	24 h	80	20	160[d]
$[Mo_2(CH_2SiMe_3)_6]$	>98	<2	300	2	1	20 h[e]

[a] Reaction conditions: organometallic compound (0.056 mmol metal content) loaded on 0.5 g of Degussa Aerosil 300, 20 ml (17.5 g, 224 mmol) of neat C_6H_6 (4000 equiv. per M), 1200–1400 psi of H_2 at 120 °C. [b] Reaction conditions: organometallic compound (0.056 mmol of metal content) loaded on 0.5 g of Degussa Aerosil 300, 2.0 g (15.6 mmol) of naphthalene (280 equiv. per M), 25 ml of n-hexane, 1400 psi of H_2 at 120 °C. [c] Products were analysed by ^1H NMR, GC and GC–MS. [d] No further hydrogen uptake after this time. [e] Product contains 94% of tetralin and 3% of naphthalene.

Table 2 Hydrogenation of benzene and substituted benzenes by silica-supported $[Nb_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$ **1a** and $[Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$ **1b** to give cyclohexanes

Substrate[a]	Catalyst	*t*/min[b]	Product (*cis*/trans)[c]
C_6H_6	**1a**	25	C_6H_{12}
C_6H_6	**1b**	55	C_6H_{12}
C_6H_5Me	**1a**	33	$C_6H_{11}Me$
C_6H_5Me	**1b**	64	$C_6H_{11}Me$
$C_6H_4Me_2\text{-}1,2$	**1a**	30	$C_6H_{10}Me_2\text{-}1,2$ (57/43)
$C_6H_4Me_2\text{-}1,2$	**1b**	75	$C_6H_{10}Me_2\text{-}1,2$ (91/9)
$C_6H_4Me_2\text{-}1,3$	**1a**	20	$C_6H_{10}Me_2\text{-}1,3$ (78/22)
$C_6H_4Me_2\text{-}1,3$	**1b**	70	$C_6H_{10}Me_2\text{-}1,3$ (92/8)
$C_6H_4Me_2\text{-}1,4$	**1a**	25	$C_6H_{10}Me_2\text{-}1,4$ (57/43)
$C_6H_4Me_2\text{-}1,4$	**1b**	65	$C_6H_{10}Me_2\text{-}1,4$ (82/18)

[a] Reaction conditions: organometallic compound (0.056 mmol metal content) loaded on 0.5 g of Aerosil Degussa 300, 26 mmol (460 equiv. per M) of substrate in 25 ml of n-hexane, 1200–1400 psi of H_2 at 120 °C. [b] Time at 120 °C; no further H_2 uptake after this time. [c] Products were analysed by ^1H NMR, GC and GC–MS, and were obtained in 100% yield.

naphthalene to a mixture of *cis–trans*-decalins (decahydronaphthalenes) with metal-dependent activity under identical conditions (Table 1). In the case of benzene hydrogenation, no intermediates were detected, but 1,2,3,4-tetrahydronaphthalene (tetralin) and various small amounts of $\Delta^{9,10}$-octalin were observed during naphthalene hydrogenations. Of particular relevance to this study is the use of the Group 5 metal alkylidyne bridged compounds $[(Me_3SiCH_2)_2M(\mu\text{-}CSiMe_3)_2M(CH_2SiMe_3)_2]$ (M = Nb, **1a**; Ta, **1b**) first synthesized by Wilkinson *et al.*[4] Besides being readily available in high yield, these crystalline compounds exhibit a high degree of thermal stability making them remarkably easy to handle for an early d-block element compound containing only metal–carbon bonds. The reaction chemistry of **1a** and **1b** with phenolic and other protic reagents has shown that stepwise substitution of the terminal alkyl groups occurs prior to cleavage of the alkylidyne bridge groups.[5] Reaction of compounds **1** with the silica support (Degussa 300, dried for 24 h at 200 °C *in vacuo*) occurs rapidly in hydrocarbon solvents to produce an orange (**1a**) or yellow (**1b**) suspension of the supported organometallic derivative. Analysis of the colourless supernatant above the impregnated support indicated the liberation of 2.0(0.5) equivalents of $SiMe_4$ per dinuclear unit. The impregnated supports carry out the catalytic hydrogenation of a variety of arene substrates in alkane solvents. Typical reaction conditions we have employed are 60–120 °C and H_2 pressures of 200–1500 psi, with the reactions being carried out in a batch mode within a high-pressure minireactor. At 120 °C and 1400 psi of H_2, hydrogenation of benzene, toluene and the three xylenes (460 equiv. per M) in hexane solvent is complete after 20–30 minutes for the niobium and 60–80 minutes for the tantalum derivative with no significant organic substrate dependence (Table 2). Neither system exhibits a high degree of stereoselectivity (*vide infra*) for hydrogenation of xylenes, although the supported tantalum compound consistently gives a higher fraction of the *cis*-isomer compared to the corresponding niobium compound. It is surprising to note that the use of the mononuclear, homoleptic tantalum alkyl $[Ta(CH_2C_6H_4Me\text{-}4)_5]$[6] leads to a less active catalyst for both benzene and naphthalene hydrogenation compared to dinuclear **1b**.

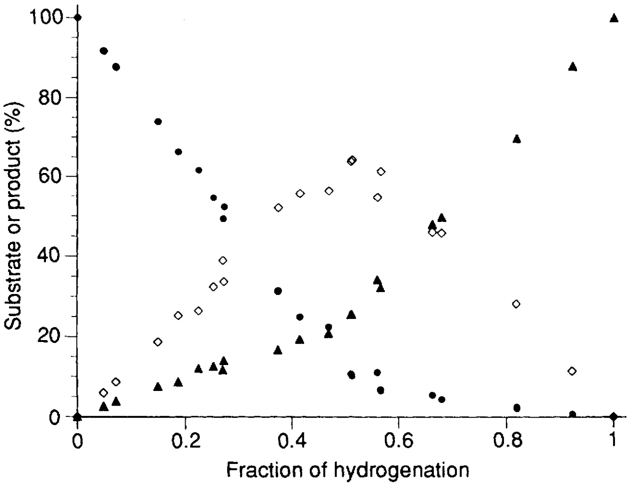

Fig. 1 Reaction profile for the hydrogenation of naphthalene in hexane solvent by supported **1b** at 90 °C. Reaction conditions are identical with those in Table 1, footnote *b*, except the temperature. Data points represent; naphthalene (●), tetralin (◇), (*cis* + *trans*) decalin (▲). The *cis*/*trans* ratio of decalin remains essentially constant at 90/10 throughout the reaction. A plot of hydrogen uptake (fraction hydrogenation) *vs*. time is linear.

A lack of stereoselectivity is also observed for the hydrogenation of naphthalene by these supported d-block metal compounds (Table 1). Furthermore, the hydrogenation of naphthalene by the supported tantalum compound **1b** at 90 °C in hexane solvent shows a lack of selectivity (Fig. 1) compared to homogeneous Group 5 systems.[2] Both tetralin and $\Delta^{9,10}$-octalin are hydrogenated to a mixture of *cis*- and *trans*-decalin by silica-supported **1a** and **1b**. The formation of *trans*-decalin from $\Delta^{9,10}$-octalin indicates that isomerization to $\Delta^{1,9}$-octalin is occurring presumably *via* β-hydrogen abstraction from an alkyl intermediate.[7] It is interesting to note that although silica-supported $[Mo_2(CH_2SiMe_3)_6]$ shows negligible activity

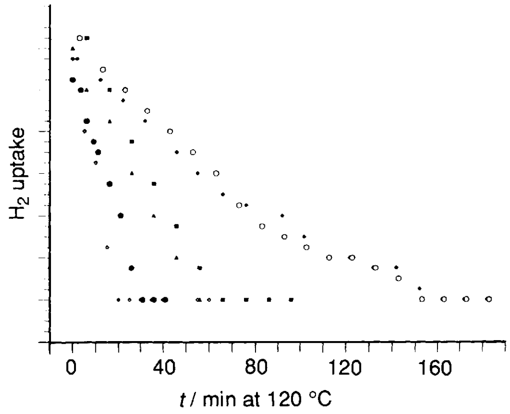

Fig. 2 Plot of hydrogen uptake *vs.* time for the hydrogenation of naphthalene under the conditions listed in Table 1, footnote *b*. [$Zr(CH_2Ph)_4$] (●), **1a** (◇), **1b** ■, [$Hf(CH_2Ph)_4$] (▲), [$Ti(CH_2SiMe_3)_4$] (○), [$Ta(CH_2C_6H_4\text{-}4Me)_5$] (◆).

for benzene hydrogenation, it slowly hydrogenates naphthalene with a reasonable selectivity for formation of tetralin.

Attempts were made to probe the stereochemistry of benzene hydrogenation utilizing [$^2H_6$]benzene as substrate. However,analysis of the product of exhaustive hydrogenation of neat C_6D_6 (20 ml) with H_2 gas at 120 °C and supported **1a** or **1b** showed a distribution of products, $C_6D_nH_{12-n}$. The partial (50%) hydrogenation (H_2) of C_6D_6 (20 ml) using **1a** showed that the unreacted benzene remained isotopically pure while the product cyclohexane had undergone extensive H–D scrambling. Furthermore, treatment of pure cyclohexane, C_6H_{12}, with supported **1a** and D_2 reagent gas (200 psi; 12 h) was found to produce deuteriated cyclohexane, $C_6D_nH_{12-n}$ indicating an ability of the supported Group 5 compounds **1** to carry out CH bond activation under the conditions of hydrogenation.

The rate of hydrogenation of various organic substrates in hexane at 120 °C has been followed by monitoring the rate of uptake of hydrogen. The rate of the reaction in hexane under 1400–1500 psi of H_2 pressure and rapid agitation approaches zero order in substrate (Fig. 2), although in the hydrogenation of neat benzene (4000 equiv. per M) the reaction rate slowed noticeably with time. The rate of hydrogenation of substrates by supported **1a** and **1b** is dependent on the hydrogen pressure. Naphthalene undergoes hydrogenation noticeably faster in hexane than cyclohexane as solvent possibly reflecting the relative solubility of hydrogen in these solvents.[8] More detailed kinetic and mechanistic studies of these systems as well as attempts to characterize surface-supported species are currently underway.

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