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Efficient transfer hydrogenation of alkynes and alkenes with methanol catalysed by hydrido(methoxo)iridium(III) complexes

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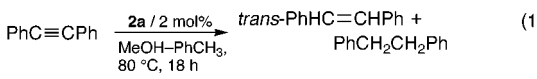
Hydrido(methoxo)iridium(III) complexes, [{Ir(H)(diphosphine)}$_2$(μ-OMe)$_2$(μ-Cl)]$^+$Cl$^-$ [diphosphine = (*R*)-BINAP **2a or = 2,2′-bis(diphenylphosphino)-1,1′-biphenyl (BPBP) **2b**] catalysed transfer hydrogenation of alkynes with methanol to give *trans*-alkenes selectively; plausible reaction pathways are also proposed.**

Catalytic transfer hydrogenation of unsaturated compounds using organic hydrogen donors such as alcohols and formic acid has widely been studied as an attractive method of reduction owing to its operational simplicity and environmentally friendly properties of the hydrogen donors.[1] Although methanol could be an exceedingly useful source of hydrogen from many viewpoints,[2] only a few reports of its use in homogeneous catalysis are available.[2,3] In addition, in contrast to the transfer hydrogenation of ketones, that of simple alkynes and alkenes by homogeneous catalysis remains relatively undeveloped.[3b,d,4] Here, we report efficient selective catalytic transfer hydrogenation of alkynes to *trans*-alkenes with soluble iridium complexes by using methanol as a hydrogen donor.

Recently we have reported that [IrCl(diphosphine)]$_2$ [diphosphine = BINAP **1a**, or 2,2′-bis(diphenylphosphino)-1,1′-biphenyl (BPBP) **1b**][5] carrying a peraryldiphosphine readily activates methanol at ambient temperature to give iridium(III) hydrido(methoxo) complexes, [{IrCl(H)(diphosphine)}$_2$(μ-Cl)(μ-OMe)$_2$]Cl [diphosphine = BINAP **2a** or BPBP **2b**].[6] In the course of the study concerning the reactivity of complexes **2** we have found that these hydrido(methoxo) complexes serve as efficient catalyst precursors for reduction of alkynes to give *trans*-alkenes using methanol as a source of hydrogen. Over-hydrogenation to alkanes was also observed. Hydrogenation proceeded in toluene–methanol (1:1, v/v) solution under fairly mild conditions at 80 °C in the presence of a catalytic amount of **2** [eqn. (1)].[7]



(1)

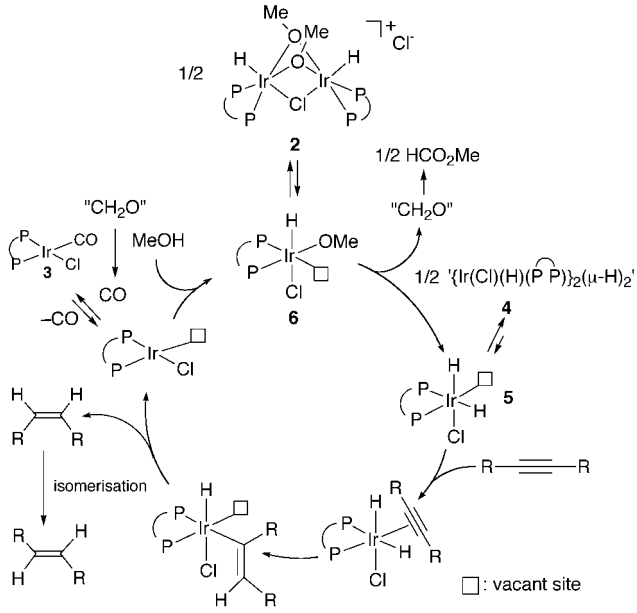
The results are summarized in Table 1. After 18 h with catalyst **2a**, diphenylacetylene was consumed completely to give 83% *trans*-stilbene and 17% 1,2-diphenylethane. Formation of *cis*-stilbene was not detected. When the reaction was stopped after 1 h, the conversion of diphenylacetylene was 29% and 12% *trans*-stilbene and 16.5% *cis*-stilbene were obtained, accompanied with 0.5% 1,2-diphenylethane. Reaction after 2 h gave the *trans*-alkene as the main product with 52% conversion. Although the reaction also proceeded under reflux > 36 h were required before complete consumption of diphenylacetylene. Hydrogenation of *trans*-stilbene gave 29% of 1,2-diphenylethane after 18 h, whereas hydrogenation of *cis*-stilbene gave the alkane in 39% yield, with almost all starting *cis*-stilbene being isomerised to *trans*-stilbene. Thus, *cis*-stilbene was hydrogenated faster than *trans*-stilbene and isomerisation of the *cis*-alkene to the *trans*-alkene proceeded much faster than its hydrogenation to the alkane in the presence of the iridium catalyst. The rate difference of the reduction between the *cis* and the *trans* isomers may reflect the difference of their binding constants,[8] resulting in high selectivity for the *trans*-alkene in the product. In other words, the initial hydrogenation product of diphenylacetylene should be *cis*-stilbene, which is isomerised to *trans*-stilbene by the iridium catalyst under the reaction conditions. Diphosphine complexes **1** can also be employed as the catalyst precursor for transfer hydrogenation. Interestingly, ethanol or propan-2-ol, generally more favorable sources of hydrogen,[2] were far less effective for the present transfer hydrogenation, and ketones were poor substrates. Acetophenone was hydrogenated in only 32% yield to give phenethyl alcohol with **2a** in toluene–methanol at 80 °C after 18 h. When the transfer hydrogenation was conducted in CD_3OD–toluene (1:1) using **2a** as a catalyst precursor, the deuterium contents of the olefinic as well as the methylene hydrogens of the products amounted to 100%. For the reaction performed in a CH_3OD–toluene (1:1), however, the corresponding values were 43 and 41%, respectively, as determined by 500 MHz ^{1}H NMR spectroscopy and GC–MS. Thus, during transfer hydrogenation hydrogens of both CH_3 and OH groups of methanol were incorporated in the products.

From the solid residue obtained from the catalytic reduction product of 1-phenylpropyne with methanol using complex **2a** as a catalyst precursor after removing all volatile materials *in*

Table 1 Transfer hydrogenation of alkynes and alkenes with MeOH catalysed by **1** and **2**[a]

Substrate	Catalyst	*t*/h	Conversion (%)	*trans*-Alkene (%)	*cis*-Alkene (%)	Alkane (%)
PhC≡CPh	**2a**	1	29	12	16.5	0.5
	2a	2	52	36	14.5	1.5
	2a	18	100	83	0	17
	2b	18	100	90	0	10
PhC≡CMe	**2a**	18	100	50	0	50
	1a	18	100	60	3	37
	1a[b]	18	25	3	22	0
	1b[c]	18	95	63	20	12
trans-PhCH=CHPh	**2a**	18	29	71	0	29
cis-PhCH=CHPh	**2a**	18	> 99	60	< 1	39
$Me(CH_2)_4C{\equiv}C(CH_2)_4Me$	**2a**	48	100	nd[d]	nd[d]	nd[d]

[a] [Substrate] = 0.5 M, [Substrate]:[Ir$^+$] = 25:1, solvent: MeOH–toluene (1:1), reaction temperature = 80 °C. Yields and conversion were determined by GLC, ^{1}H NMR and GC-MS. [b] Solvent: EtOH–toluene (1:1). [c] Solvent: Pr^{i}OH–toluene (1:1). [d] nd = not determined. Mixtures of dodecenes and dodecane were detected by GC–MS.



Scheme 1

vacuo, two iridium complexes, IrCl(CO)(BINAP) **3**[9] (major) and '{Ir(Cl)(H)(BINAP)}$_2$(μ-H)$_2$' **4** (minor),[10] were isolated. Although complex **3** showed comparable catalytic activity to that of **2a** for the transfer hydrogenation of diphenylacetylene, complex **4** was far less efficient. Methyl formate, the Tishchenko product of the by-product formaldehyde, was also detected by GC–MS in the reaction mixture. Based on these experimental results, we propose a plausible reaction pathway of the transfer hydrogenation of alkynes as well as alkenes and the isomerisation of alkenes catalysed by complex **2** (Scheme 1).[11] The real catalyst may be a nascent mononuclear dihydride species such as **5**, which dimerises to give the catalytically inactive dimer **4**. The possibility that coordination of alkyne to the monomeric hydrido(methoxo)complex **6** is the first step followed by hydride insertion to give a methoxo(vinyl) complex, however, can not be eliminated, though such species could not be detected by NMR of the reaction mixture of complex **2a** and diphenylacetylene.

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7 Catalytic transfer hydrogenation: an alkyne (2 mmol) and complex **2** (0.04 mmol) were dissolved in a mixture of methanol (2 mL) and toluene (2 mL) in a glass ampoule under argon and sealed under reduced pressure at −197 °C. The ampoule, placed in a steel pipe, was heated at 80 °C for 18 h. The reaction products were analyzed by GLC, ^{1}H NMR and GC–MS.

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9 Complex **3**: orange powder. Anal. Calc. for $C_{45}H_{32}ClIrOP_2$: C, 61.53; H, 3.67. Found: C, 61.42; H, 3.84%; Mp > 120 °C (decomp.); MS (FAB) *m/z* 878 (M^+), 850 (M^+ − CO); IR 1986 (film, ν_{CO}), 304w cm^{-1} (Nujol, ν_{Ir-Cl}); δ_P($CDCl_3$, 121 MHz) 16.5 (d, *J* 28 Hz), 22.7 (d, *J* 28 Hz); δ_C($CDCl_3$, 75 MHz) 180.7 (dd, *J* 11, 123 Hz, *C*O). Complex **3** can be quantitatively prepared from the reaction of **1** and CO.

10 Complex **4**: yellowish orange powder, IR (Nujol) 2279 (ν_{Ir-H_t}), *ca.* 1620w br cm^{-1} (ν_{Ir-H_b}); δ_H($CDCl_3$, 300 MHz) −22.38 (dd, *J* 15, 21 Hz, Ir–H$_t$) and −11.57(tt, *J* 8, 64 Hz, Ir–H$_b$); δ_P($CDCl_3$, 121.5 MHz) 3.6 (dd, *J* 9, 10 Hz) and 5.9 (dd, *J* 9, 10 Hz); MS (FAB): group of peaks centered at *m/z* 1703 resembling the simulated pattern for (M^+ − 1) (M = $C_{88}H_{68}{}^{35}Cl_2{}^{193}Ir_2P_2$). Although complex **4** could not be isolated as a pure state, on the basis of these spectral data we tentatively propose the structure '{Ir(H)(Cl)(BINAP)}$_2$(μ-H)$_2$'. Complex **4** can also be obtained as the main product by pyrolysis of complex **2a** at 80 °C in methanol–toluene.

11 For isomerisation as well as hydrogenation of alkenes, the same dihydride **5** can also act as a catalyst. Insertion of *cis*-alkene into Ir–H and subsequent β-hydrogen elimination from the hydrido(alkyl) complex gives *trans*-alkene and **5**, or reductive elimination from the hydrido(alkyl) complex gives alkane and 'Ir(diphosphine)Cl', respectively.

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