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# Highly diastereoselective dihydride formation by activation of methanol with IrCl{(*S*)-binap}($PPh_3$)

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**Reaction of [IrCl{(*S*)-binap}($PPh_3$)] {(*S*)-3} with methanol gave one of the diastereomers of the *cis,mer*-dihydride, *cis,mer-OC*-6-44-*A*-[IrCl($H_2$){(*S*)-binap}($PPh_3$)] {(*S*)-4a} stereoselectively, the structure of which was determined crystallographically, whereas the reaction of (*S*)-3 with $H_2$ produced a 1 : 1 mixture of the diastereomers of the *cis,mer*-dihydride, (*S*)-4a and *cis,mer-OC*-6-44-*C*-[IrCl($H_2$){(*S*)-binap}($PPh_3$)] {(*S*)-4b}.**

Although the stereochemistry for the formation of the dihydrides of rhodium and iridium carrying chiral ligands is of great interest in connection with their potential as asymmetric hydrogenation and its mechanism,[1] only very rare cases of detection of diastereoselective formation of dihydrides have been reported.[2–6] Even in such cases the absolute configuration of the hydride was only estimated based on spectroscopic results. Here we report a highly diastereoselective formation of the dihydride (*S*)-**4a** by reaction of [IrCl{(*S*)-binap}($PPh_3$)] {(*S*)-**3**}[7] with methanol, the absolute configuration of which was determined by X-ray analysis. Oxidative addition of dihydrogen to (*S*)-**3** gave also the same *cis,mer*-dihydrides **4** but as a 1 : 1 mixture of the diastereomers **4a** and **4b**.

Recently we have reported that iridium(I) complexes bearing perarydiphosphines [IrCl(diphosphine)]$_2$ (**1**) can activate O–H bonds easily at room temperature. For example, [IrCl(binap)]$_2$ (**1a**) reacted easily with methanol at room temperature to give the hydrido(methoxo) complex, [{Ir(H)(binap)}$_2$(μ-OMe)$_2$(μ-Cl)]Cl (**2**) in good yield,[8] which becomes an efficient catalyst precursor for transfer hydrogenation of alkynes using methanol as a hydrogen source.[9] During the studies on the reactivity of complex **1**, we have found that [IrCl(binap)]$_2$ (**1a**) reacted with 2 equiv. of $PPh_3$ to give a square-planar complex, [IrCl(binap)($PPh_3$)] (**3**) selectively as a red solid.[7] The molecular structure of (*R*)-**3** is shown in Fig. 1.† In contrast to complex **1a**, complex **3** was fairly stable in the solid state. Heating a toluene solution of complex (*S*)-**3** with large excess of methanol at 70 °C during 6 h, however, gave pale-red precipitates (67% yield) of the dihydride (*S*)-**4a**[10] as a single diastereomer. The crude reaction mixture obtained after removal of the all solvents showed almost quantitative and selective formation of the dihydride **4** containing a small amount of the other diastereomer (*S*)-**4b**[11] {(*S*)-**4a** : (*S*)-**4b** = 92 : 8}. The reaction of (*S*)-**3** with methanol proceeded even at room temperature in toluene and after 45 h gave selectively the *cis,mer*-dihydride (*S*)-**4a** in about 90% yield {(*S*)-**4a** : (*S*)-**4b** = 96 : 4} (Scheme 1). The reaction, however, is very much suppressed when excess triphenylphosphine is present. Complex (*S*)-**4a** was fully characterized by elemental analyses and spectroscopic studies. The $^1H$ NMR spectrum showed two characteristic hydride signals at $\delta$ −19.56 and −9.97; the latter signal showed one large P–H coupling indicating that the hydride is situated *trans* to one phosphorus atom while the former signal does not show any couplings larger than *ca.* 20 Hz, indicating the hydride situates *cis* to all the phosphorus atoms. The $^{31}P$ NMR spectrum measured at 35 °C showed three phosphorus signals at $\delta$ −4.7 (br m), 14.9 (dd, *J* = 16, 358 Hz) and 19.6 (dd, *J* = 11, 358 Hz) in a 1 : 1 : 1 ratio; the signal pattern indicates that the three phosphorus atoms coordinate to the central atom in a *mer* configuration. The dihydride complex showed two Ir–H stretchings (Nujol) at 2207 (*trans* to Cl) and 2083 cm$^{-1}$ (*trans* to P). Suitable crystals for X-ray analysis were obtained by recrystallization from toluene-methanol. The absolute configuration of the dihydride was concretely determined by X-ray crystallography.† The ORTEP drawing is depicted in Fig. 2. The predominant diastereomer (*S*)-**4a** obtained by the reaction of (*S*)-**3** with methanol was revealed to be the (*S*)-*OC*-6-44-*A* isomer. The long bond distance (2.363(2) Å) of Ir–P(2) indicates a strong *trans* influence of the hydride ligand. Similarly, the Ir(III)–Cl bond distance (2.505(3) Å) is long and even longer than the Ir(I)–Cl distance (2.394(2) Å) in the Ir(I) complex (*R*)-**3**. The acute P(1)–Ir–P(3) angle (167.30(9)°) reflects also the small hydride ligand. The same diastereomeric dihydride (*S*)-**4a** was also obtained selectively by the reaction of (*S*)-**2** with 2 equiv. of $PPh_3$ in a mixed solvent of methanol and toluene under reflux

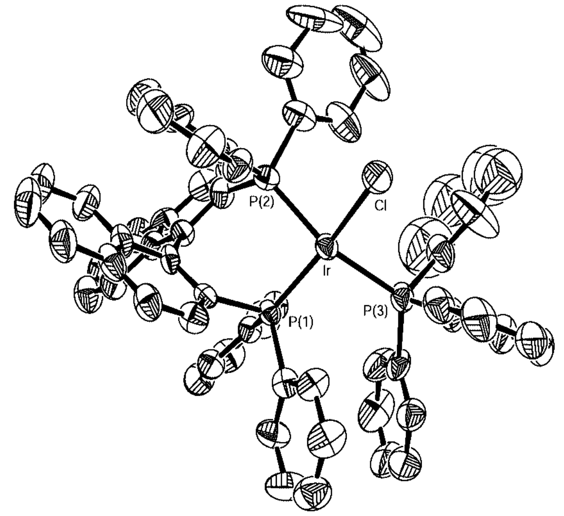
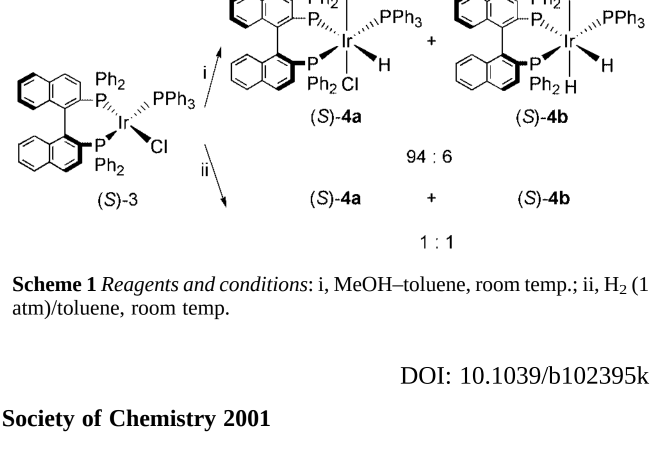


**Fig. 1** View of (*R*)-**3** showing the labeling of the heteroatoms. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°): Ir–P(1) 2.1998(19), Ir–P(2) 2.277(2), Ir–P(3) 2.305(2), Ir–Cl 2.394(2); P(1)–Ir–P(2) 91.58(7), P(1)–Ir–P(3) 99.20(8), P(2)–Ir–P(3) 157.11(8), P(1)–Ir–Cl 159.23(10), P(2)–Ir–Cl 87.76(9), P(3)–Ir–Cl 89.09(9).



**Scheme 1** *Reagents and conditions*: i, MeOH–toluene, room temp.; ii, $H_2$ (1 atm)/toluene, room temp.

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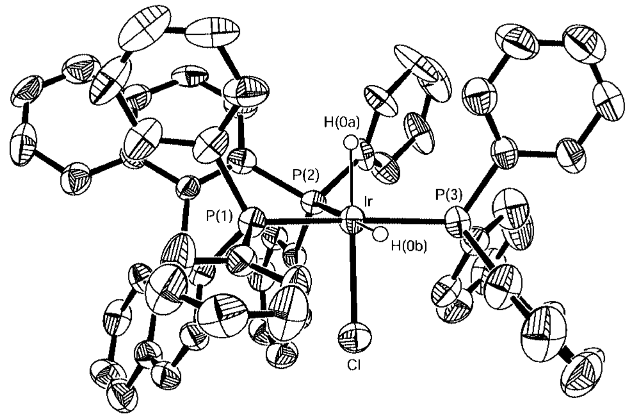
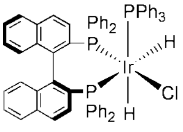


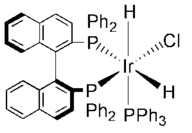
**Fig. 2** View of (*S*)-**4a** showing the labeling of the heteroatoms and the hydride hydrogen atoms. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°): Ir–P(1) 2.299(3), Ir–P(3) 2.326(3), Ir–P(2) 2.363(2), Ir–Cl 2.505(3); P(1)–Ir–P(3) 167.30(9), P(1)–Ir–P(2) 92.70(16), P(3)–Ir–P(2) 100.00(16), P(1)–Ir–Cl 88.81(10), P(3)–Ir–Cl 88.38(10), P(2)–Ir–Cl 102.98(10).

but accompanied by small amounts of several unidentified hydrides [eqn. (1)]. Hydrogenation of complex (*S*)-**3** with dihydrogen in toluene at room temperature also yielded the same *cis,mer*-dihydride **4** but as an almost 1 : 1 mixture of the two diastereomers (*S*)-**4a** and (*S*)-**4b**. These dihydrides are obtained by a concerted *cis* addition of $H_2$ along the P–Ir–Cl axis of the square planar complex (*S*)-**3**. In the reaction products obtained by oxidative addition of $H_2$ to (*S*)-**3** substantial amounts of *cis,fac*-isomer **5** resulted from *cis* addition of $H_2$ along the P–Ir–P axis of complex (*S*)-**3** and the other possible dihydride **6** could not be detected.

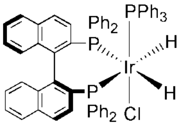
$$\underset{(S)\text{-}\mathbf{2}}{[(\mathrm{ir(H)}\{(S)\text{-binap}\})_2(\mu\text{-OMe})_2(\mu\text{-Cl})]\mathrm{Cl}} + 2\mathrm{PPh_3} \xrightarrow[\text{MeOH/toluene (v/v = 1/1)}]{\text{reflux, 39 h}} (S)\text{-}\mathbf{4a} \qquad (1)$$



(*S*)-**5a**



(*S*)-**5b**



(*S*)-**6**

Although the detailed mechanism for diastereoselective formation of (*S*)-**4a** by the reaction of (*S*)-**3** with methanol is not clear at present, the large difference of the selectivity between methanol and hydrogen may be explained as follows. Dihydride formation from the reaction of **3** with methanol could be explained by β-hydrogen elimination from the Ir–OMe group of the initial oxidative addition product of methanol, a hydrido(methoxo) complex, 'IrCl(H)(OMe)(binap)(PPh$_3$)', which is not detected in the reaction mixture. Such iridium dihydride formation from the H–Ir–OMe species has been reported.[12] Because methanol is much larger than dihydrogen, methanol approaches also only along the P–Ir–Cl axis to complex (*S*)-**3** and in addition can discriminate efficiently between the two diastereotopic planes of (*S*)-**3**, above and below the Ir(I) square plane. By inspection of a CPK model, approach of methanol from above the square plane of (*S*)-**3** described in Scheme 1 is more preferable and leads to the highly stereoselective formation of dihydride (*S*)-**4a**.[13] In contrast, the small dihydrogen molecule can not efficiently discriminate between the diastereotopic planes.

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## Notes and references

† *Crystal data* for (*R*)-**3**: $C_{62}H_{47}ClIrP_3$, $M$ = 1112.56, trigonal, space group $P3_1$ (no. 144), $a$ = 18.579(5), $b$ = 18.579(5), $c$ = 13.368(6) Å, $\alpha$ = 90, $\beta$ = 90, $\gamma$ = 120°, $U$ = 3996(2) Å$^3$, $T$ = 296(2) K, $Z$ = 3, $D_c$ = 1.387 Mg m$^{-3}$, $\lambda$(Mo-K$\alpha$) = 0.71069 Å, $\mu$ = 2.684 mm$^{-1}$, $2\theta_{max}$ = 55.0°, absorption corrections[14] ($T_{min}$ = 0.2958, $T_{max}$ = 0.4998), a linear correction was applied (24.9% decay), 12250 unique reflections including Friedel pairs ($R_{int}$ = 0.0426), direct methods (SIR97),[15] full-matrix least-squares methods (SHELXL-97),[16] refined on $F^2$. The aromatic H-atoms were included in the refinement on calculated positions riding on their carrier atoms (C(sp$^2$)–H = 0.93 Å, $U_{iso}$(H) = 1.2$U_{eq}$(C) Å$^2$). $R1/wR2$ (for 9697 reflections with $I > 2.0\sigma(I)$) = 0.0455/0.1288, $R1/wR2$ (for 12550 reflections with all data) = 0.0739/0.1429 for 581 parameters and 5 restraints, $\chi$ (Flack parameter) = −0.005(7), GOF = 1.040, $\Delta\rho$ (max./min.) = 1.513/−0.745 e Å$^{-3}$.

For (*S*)-**4a**: $C_{62}H_{49}ClIrP_3$, $M$ = 1114.57, monoclinic, space group $P2_1$ (no. 4), $a$ = 11.070(3), $b$ = 21.979(4), $c$ = 11.788(3) Å, $\beta$ = 96.50(2)°, $U$ = 2849.7(12) Å$^3$, $T$ = 296(2) K, $Z$ = 2, $D_c$ = 1.299 Mg m$^{-3}$, $\lambda$(Mo-K$\alpha$) = 0.71069 Å, $\mu$ = 2.509 mm$^{-1}$, $2\theta_{max}$ = 65.0°, absorption corrections[14] ($T_{min}$ = 0.4023, $T_{max}$ = 0.8168), a linear correction was applied (9.2% decay), 21894 reflections measured, 20525 unique reflections including Friedel pairs ($R_{int}$ = 0.0693), direct methods (SIR97),[15] full-matrix least-squares methods (SHELXL-97),[16] refined on $F^2$. Non-hydrogen atoms were anisotropically refined. The aromatic H-atoms were included in the refinement on calculated positions riding on their carrier atoms (C(sp$^2$)–H = 0.93 Å, $U_{iso}$(H) = 1.2$U_{eq}$(C) Å$^2$). Probable hydride-ligand positions were calculated at the minima of the potential energy by the program HYDEX[17] and were included as fixed contributions. $R1$ = 0.0578, $wR2$ = 0.1483, (for 8479 reflections with $I > 2.0\sigma(I)$), $R1$ = 0.2305, $wR2$ = 0.1953, (for 20525 reflections with all data), parameters = 603, $\chi$ (Flack parameter) = −0.050(9), GOF = 0.964.

CCDC reference numbers 168686 and 168687.

See http://www.rsc.org/suppdata/cc/b1/b102395k/ for crystallographic data in CIF or other electronic format.

1 P. P. Deutsch and R. Eisenberg, *Chem. Rev.*, 1988, **88**, 1147.
2 I. D. Grindnev, N. Higashi, K. Asakura and T. Imamoto, *J. Am. Chem. Soc.*, 2000, **122**, 7183.
3 B. F. M. Kimmich, E. Somsook and C. R. Landis, *J. Am. Chem. Soc.*, 1998, **120**, 10115.
4 A. Harthun, R. Kadyrov, R. Selke and J. Bargon, *Angew. Chem., Int. Ed.*, 1997, **36**, 1103.
5 A. J. Kunin, R. Farid, C. E. Johnson and R. Eisenberg, *J. Am. Chem. Soc.*, 1985, **107**, 5315.
6 J. M. Brown and P. J. Madox, *J. Chem. Soc., Chem. Commun.*, 1987, 1278.
7 T. Yamagata, A. Iseki and K. Tani, *Chem. Lett.*, 1997, 1215.
8 K. Tani, A. Iseki and T. Yamagata, *Angew. Chem., Int. Ed.*, 1998, **37**, 3381.
9 K. Tani, A. Iseki and T. Yamagata, *Chem. Commun.*, 1999, 1821.
10 *OC*-6-44-*A* isomer **4a**: $^1$H NMR ($C_6D_6$, 35 °C): $\delta$ −19.56 (m, 1H), −9.97 (dddd, $J$ = 5.2, 11.2, 22.1, 132.9 Hz, 1H), 6.3–8.1 (m, 44H), 8.20 (t, $J$ = 8.4 Hz, 1H), 8.87 (t, $J$ = 8.4 Hz, 2H). $^{31}$P NMR ($C_6D_6$, 35 °C): $\delta$ −4.7 (br m, 1P), 14.9 (dd, $J$ = 16, 358 Hz, 1P), 19.6 (dd, $J$ = 11, 358 Hz). IR(Nujol): 2207 ($\nu_{Ir-H}$), 2083 cm$^{-1}$ ($\nu_{Ir-H}$), Anal. Calc. for $C_{62}H_{49}ClIrP_3$: C, 66.81; H, 4.43. Found: C, 66.73; H, 4.54%.
11 *OC*-6-44-*C* isomer **4b**: $^1$H NMR ($C_6D_6$, 35 °C): $\delta$ −20.03 (m, 1H), −10.56 (dddd, $J$ = 5.1, 16.9, 22.2, 136.8 Hz, 1H); $^{31}$P NMR ($C_6D_6$, 35 °C): $\delta$ 1.0 (m, 1P), 4.6 (dd, $J$ = 13, 356 Hz, 1P), 7.0 (dd, $J$ = 16, 356 Hz). IR(Nujol): 2274 ($\nu_{Ir-H}$), 2119 cm$^{-1}$ ($\nu_{Ir-H}$).
12 O. Blum and D. Milstein, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 229; O. Blum and D. Milstein, *J. Am. Chem. Soc.*, 1995, **117**, 4582.
13 As one referee pointed out, a possibility that the high diastereoselectivity arises during the β-hydrogen elimination from methoxide cannot be excluded at present.
14 A. C. T North, D. C. Phillips and F. S. Mathews, *Acta. Crystallogr., Sect. A*, 1968, **24**, 351.
15 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
16 G. M. Sheldrick, , SHELXL 97, Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, 1997.
17 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.