Diastereoselective Aldol Reaction with an Acetate Enolate: 2,6-Bis(2-isopropylphenyl)-3,5-dimethylphenol as an Extremely Effective Chiral Auxiliary**

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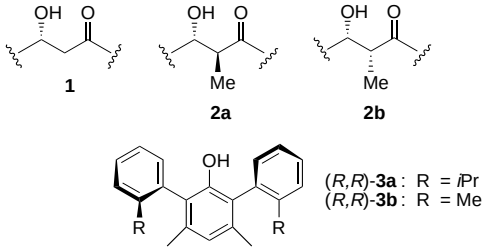
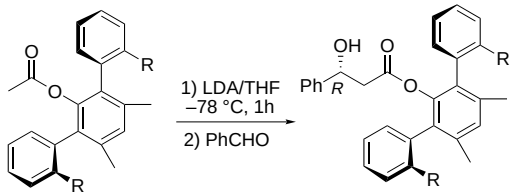
The optically active 3-hydroxycarbonyl (**1**) and 3-hydroxy-2-methylcarbonyl units (**2**) are present in numerous natural products. When covalently bound by chiral auxiliaries, acetate and propionate enolates and their variants have found widespread use in the construction of **1** and **2**. Despite



thorough investigations and a variety of approaches to structural units **2**,[1] the aldol synthesis of unit **1**[2, 3] by use of a chiral auxiliary lacks general utility due to its inherent difficulties, as suggested by Braun and others.[2] The strategy of Braun et al. to use (*R*)- and (*S*)-(2-hydroxy-1,2,2-triphenylethyl)acetate (HYTRA) is widely recognized as the most practical and elegant approach, although extremely low temperatures (ca. −130 °C) are required for satisfactory diastereoselectivity.[3d, m] More recent efforts to develop procedures which are applicable to **1** have met with only limited success.[3e–i] Here we address the potential limitations of the aldolization to **1** by utilizing the sterically hindered 2,6-bis(2-isopropylphenyl)-3,5-dimethylphenol (**3a**)[4] as an effective chiral auxiliary for an acetate enolate.

The optically active, bulky phenols (*R*,*R*)- and (*S*,*S*)-**3** were readily accessible by the previously described method.[4] Chiral acetates **4** were prepared by sequential treatment of **3** with BuLi and acetyl chloride at 0 °C in THF. The procedure shown in Scheme 1 is representative of the aldol condensation of **4a** with aldehydes. Treatment of **4a** with lithium diisopropylamide (LDA, 1.1 equiv) at −78 °C for 1 h followed by addition of benzaldehyde (1.1 equiv) gave, after stirring for 1 h and subsequent purification by column chromatography on silica gel,[5] aldol adduct **5a** in 69% yield and with greater than 97% *de*. In comparison, the sterically less and more hindered analogues **4b** and **4c** gave **5b** and **5c** with



(*R*,*R*)-**4a**: R = *i*Pr
(*R*,*R*)-**4b**: R = Me

(*R*,*R*)-**5a**: R = *i*Pr
(*R*,*R*)-**5b**: R = Me

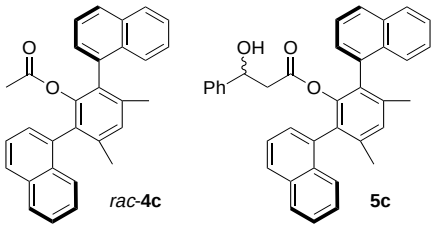
Scheme 1. Aldol reaction of chiral acetates **4a** and **4b** with benzaldehyde.

disappointingly lower *de* values of 76% and 78%, respectively (Table 1, entries 2 and 3). The effect of other solvents including Et_2O and dimethoxyethane (DME) also decreased

Table 1. Aldol reaction of chiral acetates with benzaldehyde under various reaction conditions.[a]

Entry	Chiral acetate	Base	Major product	Yield [%][b]	*de* [%][c]
1	**4a**	LDA	**5a**	69	97
2	**4b**	LDA	**5b**	58	76
3[d]	**4c**	LDA	**5c**	22	78
4[e]	**4a**	LDA	**5a**	49	81
5[f]	**4a**	LDA	**5a**	< 25	64
6	**4a**	Et_2NLi	**5a**	51	94
7	**4a**	$(CH_2)_4NLi$	**5a**	30	92
8	**4a**	LTMP[g]	**5a**	0	–
9	**4a**	LHMDS[h]	**5a**	0	–
10	**4a**	KHMDS[i]	**5a**	0	–

[a] Unless otherwise noted, the reactions were carried out with the acetate (1.0 equiv), base (1.1 equiv), and PhCHO (1.1 equiv) in THF at −78 °C. [b] Yield of isolated product. [c] In all the cases except for entry 3, the *de* value was determined by a chiral HPLC analysis (column: OB-H) after conversion of **5** into the corresponding diol. The absolute configuration at C3 of the major isomer was assigned to be *R* by comparison of the optical rotation of the diol with that reported in the literature; see T. H. Chan, K. T. Nwe, *J. Org. Chem.* **1992**, *57*, 6107. [d] Racemic **4c** was used. [e] Diethyl ether was used as solvent. [f] The reaction was performed at −50 °C with 1,2-dimethoxyethane (DME) as solvent. [g] LTMP = lithium 2,2,6,6-tetramethylpiperidide. [h] LHMDS = lithium hexamethyldisilazide. [i] KHMDS = potassium hexamethyldisilazide.



the degree of asymmetric induction (entries 4 and 5). An attempt to use less bulky bases such as Et_2NLi and $(CH_2)_4NLi$ led to high *de* values, but a decline in the yields of isolated products (entries 6 and 7). In contrast, more bulky bases gave no aldol adduct. However, about 96% of **4a** could be recovered, suggesting unsuccessful enolate generation (entries 8–10). The failure of the reaction could be attributed to the significant steric repulsion between the bulky bases and the auxiliary.

In light of the efficiency of the LDA-promoted system for **4a**, we further investigated this aldolization with a series of

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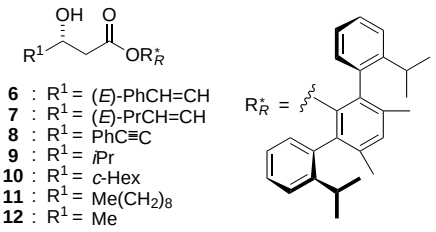
aldehydes; the results are summarized in Table 2. Excellent diastereoselectivity (94–99% *de*) was maintained for a range of alkyl-, alkenyl-, and alkynyl-substituted aldehydes. The

Table 2. Asymmetric aldol reaction of (*R*,*R*)-**4a** with various aldehydes.[a]

Entry	Aldehyde	Yield [%][b]	Product	*de* [%][c] (abs. config.)[d]
1	(*E*)-PhCH=CHCHO	77	**6**	> 99 (*R*)
2[e]	(*E*)-PrCH=CHCHO	90	**7**	95 (*R*)
3[e]	PhC≡CCHO	81	**8**	94 (*R*)
4	*i*PrCHO	62	**9**	> 99 (*R*)
5[f]	*c*-HexCHO	87	**10**	98 (*R*)
6	$Me(CH_2)_8CHO$	70	**11**	99 (*S*)
7	MeCHO	57	**12**	95 (*S*)

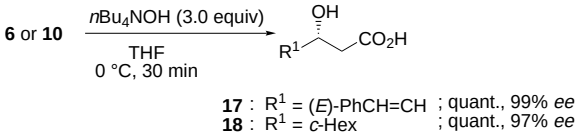
[a] Unless otherwise noted, the reactions were carried out with **4a** (1.0 equiv), LDA (1.1 equiv), and R^1CHO (1.1 equiv) in THF at −78 °C. [b] Yield of isolated product. [c] Determined by chiral HPLC or GC analyses. [d] The configuration at the carbon atom attached to the OH group was assigned by converting **6**–**12** into the corresponding products, whose optical rotations are known.[8] [e] The aldehyde was added at −100 °C. [f] Chiral acetate **4a** (1.8 equiv), LDA (1.8 equiv), and R^1CHO (1.0 equiv) were used.



diastereoselectivities and substrate generality that we observed match or exceed the best reported values with other chiral acetates or their analogues.[3d, i, m, q]

We were pleased to find reagent control,[6] in which the stereochemical preference of the chiral enolate governs the reaction stereochemistry (Table 3). For example, aldolization of a 1:1 mixture of (*S*)-**13a** and (*R*)-**13a** with (*R*,*R*)-**4a** at −78 °C gave *anti* (90% *ee*) and *syn* isomers (99% *ee*) of **14** in 49 and 41% yield, respectively.[7, 8] Thus, the absolute configuration of the emerging C_3 carbon atoms of *anti*- and *syn*-**14** are identical, and enantiofacial selectivity with respect to the aldehyde carbonyl group is consistent with all the results summarized in Table 2. When (*R*,*R*)-**4a** was replaced with (*S*,*S*)-**4a**, antipodes of **14** (*anti*- and *syn*-**15**) formed with equal effectiveness. The two major diastereomers out of four possible stereoisomers in each reaction were easily separated by chromatography. Similarly, 2-benzyloxypropanal (*rac*-**13b**) gave predominantly a 1:1 mixture[7] of *anti*- and *syn*-**16**, indicating again that chirality transfer occurred solely from (*R*,*R*)-**4a** and not from **13**.

The alkaline hydrolysis of adducts **6** and **10** proceeded smoothly with Bu_4NOH[9] in THF at 0 °C for 30 min to yield carboxylic acids **17** (99% *ee*) and **18** (97% *ee*) accompanied by a nearly quantitative amount of **3a**, which could be reused without loss of the optical purity (Scheme 2).[8] There was negligible stereoisomerization at the stereogenic centers due to a retro-aldol reaction.



Scheme 2. Alkaline hydrolysis of aldolates **6** and **10** derived from (*R*,*R*)-**4a**.

The X-ray crystal structure of (*R*,*R*)-**4a**[10] (Figure 1) revealed that the carbonyl plane is oriented perpendicular to the central phenyl plane of the auxiliary, thus minimizing the steric interaction with the two isopropylphenyl groups. In all the present cases, a large preference of the enolate of (*R*,*R*)-**4a** for attack on the *re* face of aldehydes was observed. We suggest two possible transition states—that is, twist boat[11] (A) and acylic models (B; Figure 2)—based on the X-ray

Table 3. Asymmetric aldol reaction of **4a** with racemic α-substituted propanal.[a]

Acetate	*rac*-Aldehyde	Conditions T [°C]	t [h]	Products[b, c]
(*R*,*R*)-**4a**	Me, CHO, Ph — *rac*-**13a**	−78	4	*anti*-**14** 49% (90% *ee*); *syn*-**14** 41% (99% *ee*)
(*S*,*S*)-**4a**	*rac*-**13a**	−100	0.5	*anti*-**15** 37% (95% *ee*); *syn*-**15** 27% (>99% *ee*)
(*S*,*S*)-**4a**	Me, CHO, OBn — *rac*-**13b**	−78	3	*anti*-**16** 39% (94% *ee*); *syn*-**16** 38% (98% *ee*)

[a] The reaction was carried out with the acetate (1.8 equiv), aldehyde (1 equiv), and LDA (1.7 equiv) in THF under the indicated conditions. [b] Yield of isolated, purified products. [c] Enantiomeric excess (*ee*) with respect to the two vicinal stereogenic carbon centers. The absolute and relative configurations were established by comparison with authentic materials; see reference [8].

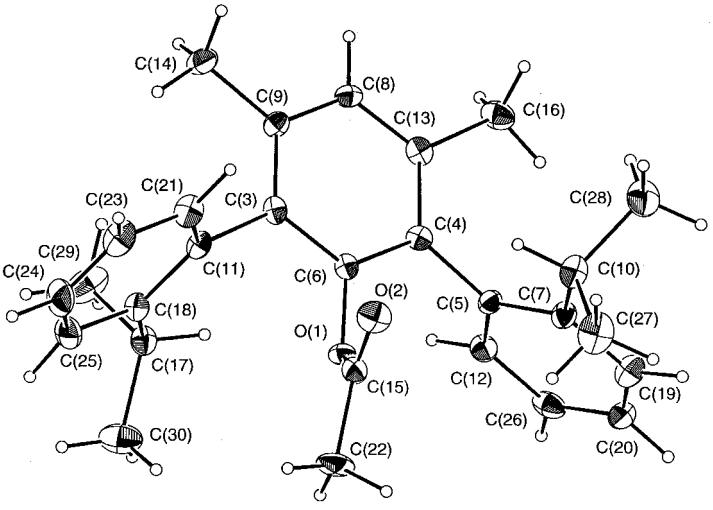


Figure 1. The X-ray crystal structure of (*R*,*R*)-**4a** (ellipsoids at the 15% probability level).

crystal structure and by taking into consideration the striking influence of the *i*Pr groups of (*R*,*R*)-**4a**. Whichever path is used, attack on the *re* face should be favored for the enolate addition.

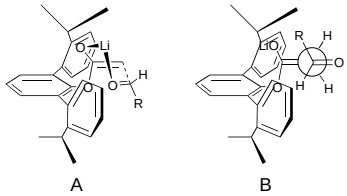


Figure 2. Proposed structure for the transition state of the aldolization: twist-boat (A) and acylic models (B).

In summary, we have successfully devised chiral auxiliary **3a** for the diastereoselective aldol reaction of an acetate with aldehydes. The present aldol system in which steric factors of **4a** predominate appears to have enhanced potential for providing high levels of diastereofacial selectivity. The ease of operation, mildness of the reaction conditions, the availability of both the enantiomers of the acetate, and substrate generality render this system advantageous and practical.

Experimental Section

The reaction of (*R*,*R*)-**4a** with benzaldehyde is representative. To a cooled (−78 °C) solution in THF of LDA—which was prepared by treatment of *i*Pr$_2$NH (77 μL, 0.55 mmol) in THF (1.0 mL) with a 1.59 M solution of *n*BuLi (0.35 mL, 0.55 mmol) in hexane at 0 °C for 30 min—was added a solution of (*R*,*R*)-**4a** (200 mg, 0.50 mmol) in THF (1.0 mL) under an argon atmosphere. After 1 h of stirring, benzaldehyde (56 μL, 0.55 mmol) was added, and the mixture was stirred at −78 °C for 1 h. The reaction mixture was quenched with H_2O at −78 °C and, after being allowed to stir at room temperature for 15 min, extracted with diethyl ether. The organic layer was dried over Na_2SO_4. Evaporation of the solvents and purification of the crude mixture by column chromatography on silica gel (diethyl ether/hexane 1/50 → 2/1) gave (*R*,*R*)-**5a** (175 mg, 69 % yield) as a colorless solid. (*R*,*R*)-**5a** (Table 1, entry 1): IR (KBr): $\tilde{\nu}$ = 3578, 2961, 1763, 1475 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 – 7.03 (m, 14H), 4.49 – 4.46 (m, 1H), 2.72 (br, 2H), 2.09 (s, 6H), 2.45 – 1.92 (m, 2H), 1.75 (dd, 1H, J = 3.6, 2.0 Hz), 1.10 (br, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 147.5, 146.2, 141.9, 136.8, 134.4, 131.8, 130.3, 129.0, 128.2, 1218.1, 127.4, 125.5, 125.3, 125.1, 69.8, 43.5, 30.0, 24.2, 20.1; elemental analysis calcd for $C_{35}H_{38}O_3$: C 82.97, H 7.56; found: C 82.88, H 7.76; $[\alpha]_D$ = −5.3 (c = 1.00, $CHCl_3$).

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[5] The crude samples of **5** – **12** and **14** – **16** were also subjected to HPLC analyses according to the procedures described in reference [8]. The *de* and *ee* values obtained were identical to those listed in Tables 1 – 3.

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[8] The *ee* or *de* values of **6**, **8**, **10,** and **14** – **16** were determined by chiral HPLC analyses [HPLC column (Daicel, Ltd.): OB-H for **14** and **15**; OD-H for **6** (i.e., **17**), **8**, and **16**; AS for **10** (i.e. **18**)] after conversion into the corresponding methyl esters by hydrolysis with *n*Bu$_4$NOH/THF and subsequent methylation with $Me_3SiCH_2N_2$. The *de* values of **7** and **11** were established by HPLC analyses [HPLC column (Daicel, Ltd.): OD-H for **7**, doubly arrayed AD for **11**]. Authentic samples for **7** and **11** were synthesized as follows: 1) oxidation of **7** or **11** with Dess – Martin periodinane to give the corresponding β-oxoesters, 2) reduction of the ketone moiety with $NaBH_4$ to yield a diastereomixture (ca. 1:1) of the starting β-hydroxyesters. The *de* values of **9** and **12** were determined by chiral GC analyses of the corresponding diol of **9** and the bis(trifluoroacetate) of the corresponding diol of **12** [GC column (Astecs, Ltd.): γ-TA]. For the relative stereochemistry of **14** and **15**, see a) T. Matsumoto, I. Tanaka, K. Fukui, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3378; the absolute configurations of **14** and **15** were unambiguously established by comparison with authentic material, which was prepared by treatment of (*R*,*R*)-**4a** with (*S*)-**13a** (ca. 80 % *ee*); for **16**, see b) Z. Pakulski, A. Zamojski, *Tetrahedron* **1995**, *51*, 871; for **8** and **10**, see c) Y. Hiraga, W, Shi, D. I. Ito, S. Ohta, T. Suga, *J. Chem. Soc. Chem. Commun.* **1993**, 1367; for **9**, see: d) B. E. Rossiter, K. B. Sharpless, *J. Org. Chem.* **1984**, *49*, 3707; for **6** and **7**, see reference [3h]. The diol derived from **12** is commercially available.

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[10] The crystals of (*R*,*R*)-**4a** were grown from MeOH/H_2O at 20 °C. Crystal data: space group $P2_12_12_1$, a = 8.738(1), b = 12.727(1), c = 22.386(2) Å, $\alpha = \beta = \gamma = 90.00°$, V = 2489.6(3) Å^3, Z = 4, ρ_{calcd} = 1.065 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 0.0652 mm^{-1}, 1079 reflections, $R1$ = 0.073, $wR2$ = 0.110, GOF = 3.691. The data were collected on a DIP-2030 (MacScience, Ltd.) imaging-plate diffractometer equipped with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The struc-

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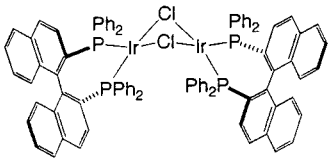
ture was solved by direct methods (maXus) and refined with all data by full-matrix least squares on *F*. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in idealized positions and included in the refinement. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102228. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] It was proposed that the boron enolates of α-unsubstituted ketones favor the more stable U form over the W form by 1–2 kcal mol^{-1}. Similarly, it is conceivable that the bulky phenoxy group of the enolate of **4a** renders the U form most likely, and gives a twist-boat transition structure: a) C. Gennari, R. Todeschini, M. G. Beretta, G. Favini, C. Scolastico, *J. Org. Chem.* **1986**, *51*, 612; b) R. W. Hoffmann, K. Ditrich, S. Froech, *Tetrahedron* **1985**, *41*, 5517; see also reference [2b].

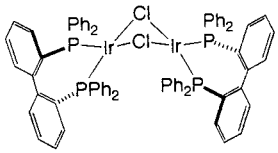
Facile Oxidative Addition of O–H Bonds of Methanol and Water to Ir^{I} Complexes Having Peraryldiphosphane Ligands**

Kazuhide Tani,* Aika Iseki, and Tsuneaki Yamagata

Studies on the oxidative addition of alcohol and water to transition metal complexes leading to the formation of hydrido(hydroxo) and hydrido(alkoxo) complexes, respectively, have received much attention for the past decade due to their potential relevance to catalysis.[1] In particular hydrido(alkoxo) complexes of late transition metals have often been postulated as intermediates or transition states in the catalytic hydrogenation of carbonyl compounds[1a] and catalytic hydrogen transfer reactions.[2] Isolation or detection of such complexes, however, is rare, and their chemistry remains relatively unexplored. About a decade ago we isolated and characterized a hydrido(alkoxo) complex of iridium as a model complex of the reaction intermediates for the rhodium-catalyzed hydrogenation of carbonyl compounds.[3] Milstein and his co-workers reported their efforts on the oxidative addition of hydrogen–heteroatom bonds to rhodium and iridium leading to hydrido(alkoxo) and hydrido(hydroxo) complexes, among others.[4] In addition the isolation of a few hydrido(alkoxo) complexes[5] and hydrido(hydroxo) complexes[1d, 5d] of late transition metals has also been reported. Almost all of these complexes, however, bear basic peralkylphosphane ligands or an electron-donating Cp* ligand (Cp* = C_5Me_5). We have found that dinuclear Ir^{I} complexes [IrCl(diphosphane)]$_2$ carrying even peraryldiphosphanes that are not so strongly electron donating (diphosphane = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (binap), see **1a**, or 2,2′-bis(diphenylphosphanyl)-1,1′-biphenyl (bpbp), see **1b**)[6, 7] can easily activate protic molecules (MeOH or H_2O) at ambient temperature.

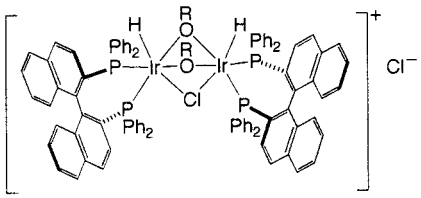


1a



1b

Upon treatment of a solution of the extremely air-sensitive complex **1a** in toluene with a large excess of methanol, the color changed immediately from deep red to pale yellow. After the reaction mixture had been stirred at room temperature for several hours, the solvents were removed in vacuo to give quantitatively the almost pure hydrido(methoxo) complex **2a** as air-stable and thermally stable pale yellow microcrystals. The formulation was supported by the elemental analyses (see Table 1 and the supporting information).



2a: R = Me
3a: R = H

The ^{31}P NMR spectrum of **2a** exhibits two doublets at $\delta = -15.2$ and -1.8 (^2J(P,P) = 19 Hz) in a 1:1 ratio, indicating the presence of two nonequivalent phosphorus atoms. The presence of terminal hydrido ligands was suggested by the IR ($\tilde{\nu}$(Ir–H) = 2270 cm^{-1}) and ^{1}H NMR spectra ($\delta = -23.10$ (dd, ^2J(H,P) = 18, 23 Hz)). The methoxy methyl protons appear at $\delta = 2.63$ as a triplet (^4J(H,P) = 3.4 Hz). The signal is more than 1 ppm upfield of the analogous signals of the mononuclear iridium complexes *mer-cis*-[Ir(Cl)(H)(OMe)(PEt$_3$)$_3$] ($\delta = 4.01$)[4d] and *cis*-[Ir(H)(OMe)(PMe$_3$)$_4$]$^+$PF$_6^-$ ($\delta = 3.637$)[4a] and appears at 0.55 ppm higher field than even that of the Ir^{I}-methoxo complex [Ir$_2$(μ-OMe)$_2$(cod)$_2$] ($\delta = 3.28$; cod = 1,5-cyclooctadiene).[8] This may be due to the diamagnetic shielding by a benzene ring of the diphenylphosphanyl moiety of the binap ligands (vide infra). Complex **2a** is much more thermally stable than these monomeric complexes. The ^{1}H NMR spectrum indicates the presence of a molecule of solvated methanol: a doublet at $\delta = 3.38$ ($J = 5.6$ Hz) for the methyl protons and a quartet at $\delta = 1.62$ for the OH proton. This may indicate strong hydrogen bonding between the chloro bridge and the solvated methanol even in solution (vide infra).[9] Exchange between the methoxo and the

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