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Transfer Hydrogenation of Ketones and Activated Olefins Using Chelating NHC Ruthenium Complexes

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N-Heterocyclic carbene (NHC) ruthenium complexes consisting of different donor substituents attached to the NHC ligand efficiently catalyse the transfer hydrogenation of ketones and of activated olefins in α,β-unsaturated ketones to give saturated alcohols. The most active catalyst precursor contains a tethered olefin as a hemilabile donor site. This complex also converts nitriles and, depending on the reaction conditions, either benzylamines are produced by means of transfer hydrogenation, or amides from formal addition of H_2O. Kinetic analysis of the double hydrogenation of α,β-unsaturated ketones indicates fast isomerisation of the enol intermediate to its saturated ketone tautomer prior to the second hydrogenation.

Introduction

Catalytic C–H bond making and breaking is one of the most useful synthetic applications of organometallic chemistry. In most hydrogenation[1] and isomerisation reactions,[2] the catalytically active species is a transition-metal hydride which is often generated in situ. Various strategies have been investigated to generate such reactive M–H intermediates including the oxidative addition of molecular hydrogen, C–H bond activation of a substrate and hydride abstraction from a hydrogen source such as a primary or secondary alcohol, amine or formic acid.[3] This latter method, viz. the abstraction of hydrogen from a donor molecule, constitutes a key step in transfer hydrogenation,[4] an alternative approach to direct hydrogenation which avoids the use of hazardous H_2 gas.

Recently, we have shown that Ru(arene) complexes containing a bidentate chelating *N*-heterocyclic carbene (NHC) ligand are effective catalyst precursors for the direct hydrogenation of olefins using H_2 (complexes **1**–**4**, Figure 1).[5] The chelating group in these complexes has a pronounced effect on the catalytic activity and the stability of the complex. While the olefin donor group in **1** was rapidly hydrogenated, thus inducing complex decomposition and predominantly heterogeneous hydrogenation, the carboxylato group in **2** markedly increased the stability of the complex. Owing to the presence of the carboxylato group, both homolytic dihydrogen activation, typically by oxidative addition and RuH_2 formation, or heterolytic dihydrogen cleavage across the Ru–O bond may be surmised. Heterolytic cleavage and involvement of a ruthenium monohydride intermediate should be facilitated if the source of dihydrogen is strongly polarised. For example in *i*PrOH, hydrogen is formally provided through a proton, bound to oxygen, and a hydride-like carbinol hydrogen.[4] Based on this hypothesis and considering the privileged role of Ru(arene) scaffolds in (transfer) hydrogenation,[3b,3c,6] and specifically the success of the corresponding NHC-containing complexes in hydrogen transfer reactions,[7] we became interested in probing the activity of complexes **1**–**4** in transfer hydrogenation. A particularly intriguing aspect was the possibility of using a single complex for either direct or transfer hydrogenation of substrates. Despite the conceptual analogy of these two hydrogenation processes, only few systems are known that exhibit such dual activity.[8]

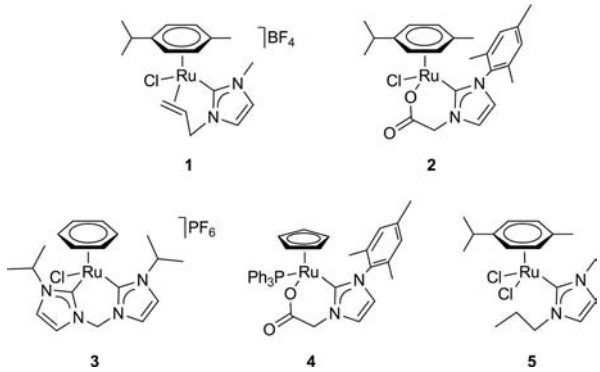

Figure 1. Chelating NHC ruthenium complexes **1**–**4** and monodentate carbene ruthenium complex **5**.

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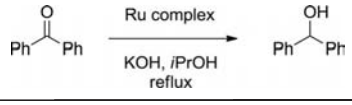
Results and Discussion

Transfer Hydrogenation of Ketones

Preliminary tests concentrated on evaluating the transfer hydrogenation activity of complexes **1**–**4** by using benzophenone as a model ketone. Standard transfer hydrogenation conditions were used,[4] viz. refluxing *i*PrOH as a hydrogen source and KOH as an activator (substrate/base/complex, 100:10:1; Table 1). Distinct differences in catalytic hydrogen transfer activities were observed for these complexes. While complete conversion was reached with all complexes apart from **4** after extended reaction times, complex **1** was most active (> 90% after 5 h). Using a carboxylato tether as in complex **2** decreased the conversion to 75% and an even lower conversion (63%) was noted after 5 h with the dicarbene complex **3**. Changing the Ru(arene)Cl scaffold in complex **2** to a $RuCpPPh_3$ fragment was disadvantageous and complex **4**, consisting of the same carboxylato-functionalised NHC ligand as **2**, displayed poor activity, reaching a modest 32% conversion after 24 h.

Table 1. Catalytic transfer hydrogenation of benzophenone.[a]



Entry	Catalyst	Chelating group	Conversion (time)	
1	**1**	olefin	90% (5 h)	98% (24 h)
2	**2**	COO^-	75% (5 h)	98% (24 h)
3	**3**	NHC	63% (5 h)	98% (24 h)
4	**4**	COO^-	9% (5 h)	32% (24 h)
5[b]	**1**	olefin	59% (10 min)	96% (30 min)
6[b]	**5**	Cl^-	36% (10 min)	63% (30 min)
7[b]	**5** + $AgBF_4$	(solvent)	59% (10 min)	79% (30 min)

[a] General conditions: substrate/KOH/catalyst, 100:10:1, conversions determined by ^1H NMR spectroscopy or GC–MS analysis. [b] In sealed Schlenk tube with degassed solvent.

The reaction conditions were further optimised for complex **1** (which showed the highest activity). The hydrogen transfer rate increased substantially upon degassing the solvent and upon performing the reaction in a gas-tight tube under an inert atmosphere and at 90 °C. Under these conditions, complete conversion was reached after less than one hour (Table 1 entry 5). No induction time was noted. After 10 min, 59% conversion was achieved, which corresponds to an approximate turnover frequency at 50% conversion TOF_{50} of ca. 360 h^{-1}. This rate is competitive with other recently reported ruthenium-carbene complexes,[7,9] though considerably lower than the most active transfer hydrogenation catalysts, which have $TOF_{50} > 10{,}000$ h^{-1}.[10]

Since hydrogenation of the olefinic tether may constitute a potential catalyst (de)activation,[11] complex **5**, comprised of an *n*-propyl wingtip group, was investigated as the saturated version of **1** (cf. Figure 1). Complex **5** was synthesised by a transmetallation procedure and was characterised spectroscopically as well as by X-ray diffraction (Figure 2).[12] The pertinent bond lengths [Ru1–C11 2.063(2)] and angles are within expected ranges.[13] Under identical reaction conditions, complex **5** was a considerably less active hydrogen transfer catalyst, achieving 36% conversion after 10 min (Table 1, entry 6). This performance corresponds to an estimated TOF_{50} of ca. 150 h^{-1}. Attempts to introduce a labile ligand into complex **5** in order to mimic the hemilability of the olefin donor in complex **1** improved the catalytic activity. For example, reaction of complex **5** with $AgBF_4$ allowed for substitution of a ruthenium-bound chloride in **5** by a solvent molecule and an essentially non-coordinating anion. The resultant complex showed an initial activity in transfer hydrogenation that compares well with that of complex **1** (entry 7), though completion is not reached within 30 min. Functionalising the ruthenium–carbene unit with an olefinic donor group seems to impart a proper balance of lability, entailing swift activation of the catalyst precursor, and stability of the catalytic resting states towards undesired decomposition. These studies thus underline the relevance of donor stabilisation as a concept in NHC transition-metal catalysis.[14]

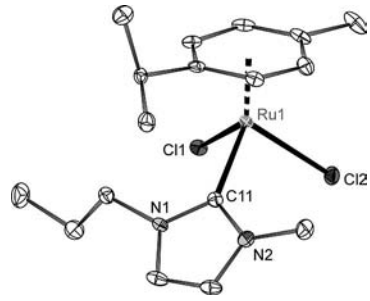


Figure 2. ORTEP representation of complex **5** (50% probability ellipsoids, hydrogen atoms, cocrystallised CH_2Cl_2, and the second crystallographically independent complex molecule omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru1–C11 2.063(2), Ru1–Cl1 2.4297(6), Ru1–Cl2 2.4437(6), C11–Ru1–Cl1 88.83(7), C11–Ru1–Cl2 88.68(7), Cl1–Ru1–Cl2 85.15(2).

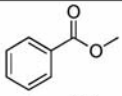
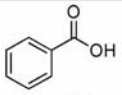
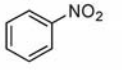
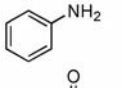
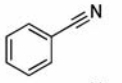
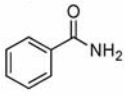
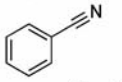
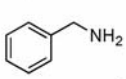
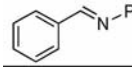
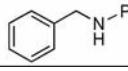
The appreciable catalytic activity of complex **1** strongly suggests that the crucial ruthenium hydride intermediate is not only accessible under direct hydrogenation conditions, but also by transfer hydrogenation.[15] We therefore extended our studies to the hydrogenation of other functional groups and activated C=C bonds, which were successfully converted by direct hydrogenation using complexes **1**–**4**.[5]

Transfer Hydrogenation of Other Functional Groups and Activated Olefins

Transfer hydrogenation of esters, nitro, and cyano groups met limited success (Table 2). The ester group in methyl benzoate appeared to be unreactive and the conversion to benzoic acid most likely ensued from saponification due to the presence of aqueous KOH as an additive. Only low activity was noted for the transfer hydrogenation of nitrobenzene to aniline. With benzonitrile, however, clean formation of benzamide occurred. Although this reaction typically requires a large excess of H_2O to achieve substantial conversions,[16] complex **1** gave quantitative products after 24 h in the presence of only 2.5 mol equiv. of H_2O relative

to the substrate. Hydrogenation of benzonitrile to benzylamine was not observed under these conditions.[17] When aqueous KOH was replaced by anhydrous *t*BuOK, transfer hydrogenation to benzylamine took place, albeit only in low yields. This low performance presumably originates from strong substrate coordination to the ruthenium centre, rather than catalyst inhibition by the intermediate imine.[10] For example, *N*-benzylideneaniline is fully converted within 24 h, yielding predominantly the hydrogenated *N*-benzylaniline. In addition to this major product, minor quantities of aniline and benzylamine were also observed, both resulting from C–N bond cleavage.[18] Obviously, nitriles bind less reversibly to the ruthenium centre than imines, which is in agreement with the high affinity of ruthenium(II) for the cyano group.

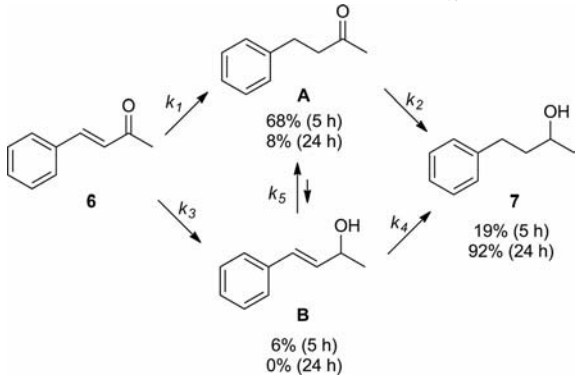
Table 2. Catalytic transformation of functional groups under transfer hydrogenation conditions using complex **1**.[a]

Substrate	Product	Conversion
		15 %
		7 %
		97 %
		13 % [b]
		60 % [c]

[a] General conditions as in Table 1 using complex **1** as catalyst precursor and degassed solvents in sealed vessels; conversions after 24 h. [b] *t*BuOK instead of aq. KOH. [c] Final reaction mixture also contained benzylamine (22%), aniline (18%) and unreacted imine (1%).

Transfer hydrogenation has been widely used to reduce not only carbonyl functions but also C=C double bonds conjugated to an electron-withdrawing group such as a carbonyl, ester, acid, nitro or cyano.[19] Hence, complex **1** was tested in the transfer hydrogenation of the α,β-unsaturated ketone **6** as an activated olefin. Under optimised reaction conditions, double transfer hydrogenation to 4-phenylbutan-2-ol (**7**) took place (91% after 5 h, Scheme 1). This product selectivity is in contrast to that observed in a study using a close analogue of complex **5**, which revealed predominant formation of the saturated ketone **A**.[7b]

In an attempt to investigate the pathway of the enone reduction in more detail, transfer hydrogenation was performed in air to deliberately decelerate the catalyst activity (i.e. suboptimal conditions, Table 1). Time-dependent monitoring of the reaction using GC–MS analysis and ^{1}H NMR spectroscopy consistently revealed the presence of the monohydrogenated ketone **A** as the prevailing intermediate, indicated by the diagnostic multiplets at δ_H = 2.9 and 2.75



Scheme 1. Transfer hydrogenation of benzylideneacetone (**6**). Rate constants k refer to the observed rate constants k_{obs}.

and the singlet at δ_H = 2.15. Additionally, enol **B** was detected as a minor component at an early stage of the reaction.

A time profile of the reaction is depicted in Figure 3. Accordingly, intermediate **A** reached a maximum concentration of 68% after 5 h. After 24 h, the starting material and intermediate **B** were completely consumed and the fully hydrogenated alcohol **7** was the major product along with traces of residue **A** (8%). While some catalysts have been reported to be inactive in converting the enol intermediate **B** and to yield mixtures,[19c,20] the catalyst derived from **1** is active towards both intermediates **A** and **B**.[10c]

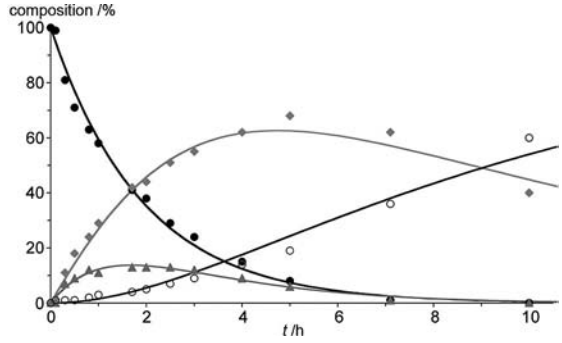


Figure 3. Time-dependent monitoring of the transfer hydrogenation of **6** (●) by GC–MS and evolution of products **A** (◆), **B** (▲) and **7** (O). Solid lines correspond to fitted rate constants using Berkeley-Madonna software upon suppressing direct hydrogenation of the enol intermediate **B** to **7**.

The activity profile suggests that both intermediates **A** and **B** are suitable substrates for a second transfer hydrogenation or, alternatively, that isomerisation between the two intermediates occurs and one substrate is preferentially hydrogenated.[21] The latter model may be supported by the fact that the rate for the formation of **A** is comparable to that of benzophenone hydrogenation (Table 1), thus suggesting a direct formation of **A** from **6**. Intermediate **A** may further accumulate as a result of keto-enol isomerisation from enol **B** with an equilibrium constant that seems to largely favour the keto isomer.[2] The reaction profile would be expected to be similar also in the former model, assuming that formation of **A** is favoured over the formation

of **B** to such an extent that, in combination with faster hydrogenation of **B** than **A** to the final product, the enol intermediate concentration falls below detection limits after some time. Kinetic modelling was therefore used to shed further light on this double transfer hydrogenation process. Taking into account the considerations outlined above, two different hypotheses were tested using the Berkeley-Madonna software.[22] In the first one, isomerisation between intermediates **A** and **B** was considered to be negligible (k_5 = 0 in Scheme 1),[23] implying that intermediates **A** and **B** were hydrogenated directly to the saturated product **7**. In the second model, isomerisation was enforced and instead, hydrogenation of the C=C bond in intermediate **B** was discarded (k_4 = 0), i.e. all enol intermediate isomerises to the saturated ketone **A** prior to the second transfer hydrogenation step. Only the second model succeeded in appropriately reproducing the time-dependent concentrations of all four components during the reaction (Figure 3). Upon suppressing the isomerisation process, only the concentrations for starting material and the final product were simulated properly while the intermediates showed a poor match with the observed data.[24]

Based on the best fitting kinetic model, the rate constants for the hydrogenation of the keto functionality is only slightly faster than that of the conjugated olefin (k_1 = 0.299, k_3 = 0.222). Transfer hydrogenation of the ketone in **A** is, however, substantially slower (k_2 = 0.108) than in the conjugated system (viz. k_3, formation of **B** from **6**). By far the fastest process is the isomerisation of the enol **B** into the saturated ketone intermediate **A** (k_5 = 0.672). Different mechanisms have been proposed for this enol-to-ketone isomerisation,[2] including transient hydrogenation (reductive process), transient dehydrogenation (oxidative process) and direct isomerisation (probably by means of an allylic intermediate). The former two processes seem unlikely in the system studied here since the reaction conditions strongly disfavour transfer dehydrogenation. The oxidative process here would involve the rebuilding of **6**, which is not competitive to the oxidation of *i*PrOH, the latter being present in large excess as a solvent.

Transfer hydrogenation of pure **B**[25] provided further support for the proposed isomerisation process. Time-dependent monitoring of the reaction indicated rapid consumption of the allylic alcohol (75% after 10 min) and concomitant formation of the saturated ketone **A** (23%), while the hydrogenated product **7** was present only in traces. The concentration of **7** exceeded 10% after only about 1 h. The kinetic analyses are in agreement with a consecutive reaction involving isomerisation and subsequent hydrogenation. The best fit revealed an approximate 2:1 ratio of the two rate constants, which is slightly lower than that determined for these two steps in the more complex reduction of **6**, a result that may be rationalised by the different starting materials, i.e. free allyl alcohol vs. precoordinated (and perhaps deprotonated) **B** when generated from **6**.

In line with the kinetic model, transfer hydrogenation of 4-*tert*-butylstyrene as a nonisomerisable analogue of intermediate **B** proceeded sluggishly. A moderate conversion of 18% was accomplished after 24 h with complex **1** as the catalyst precursor. While a remarkable TOF of 10 h^{-1} was noted for the first 30 min, the overall reaction rate is much too low to account for a direct hydrogenation of intermediate **B** without prior isomerisation to the ketone **A**. Apparently, the electron-withdrawing nature of the phenyl substituent in styryl derivatives does not sufficiently polarise the olefinic C=C bond. The lower catalytic activity of **1** towards styrene when compared with **6** may also suggest a critical role of the oxygen lone pair for the formation of a classical η^3-allyl or a η^3-oxoallyl intermediate.[26]

Conclusions

We have demonstrated that ruthenium NHC complexes that have previously shown activity in catalysing direct hydrogenation and the activation of H_2 are also efficient catalysts for the transfer hydrogenation of ketones. Depending on the reaction conditions, nitriles and α,β-unsaturated ketones were successfully converted as well. Kinetic analysis of the enone reduction suggests that the ruthenium NHC complexes not only catalyse transfer hydrogenation but also induce a rapid keto-enol tautomerisation. Such isomerisations may become useful for H/D exchange reactions and also for the transfer hydrogenation of less activated substrates. Expansion of our results in these directions is currently in progress.

Experimental Section

General: The preparation of complexes **1**–**4**[5] and 3-methyl-1-propylimidazolium bromide[27] was reported previously. CH_2Cl_2 was dried with P_2O_5 and distilled before use. Anhydrous *i*PrOH was purchased in 99.5% purity and used without further treatment. All other reagents were commercially available and were used as received. Column chromatography was carried out on Apollo Scientific ZEOprep 60 (40–63 microns) column. All ^{1}H NMR spectra were recorded at 25 °C on Bruker or Varian spectrometers and referenced to residual proton solvent signals (δ in ppm, J in Hz). High resolution mass spectrometry was carried out with a Micromass/Waters Corp. (USA) liquid chromatography time-of-flight spectrometer equipped with an electrospray source. GC–MS analyses were performed on a GCT Premier GC–MS instrument (Micromass/Waters Corp. USA) using a temperature gradient.

Synthesis of Complex 5: A suspension of 3-methyl-1-propylimidazolium bromide (270 mg, 1.32 mmol) in CH_2Cl_2 (10 mL) was placed under an N_2 atmosphere and degassed by means of three freeze-pump-thaw cycles. Ag_2O (153 mg, 0.66 mmol) was added and the reaction mixture was stirred in the dark for 16 h. The crude product was filtered through a pad of Celite. The filtrate was concentrated to 5 mL and added to a solution of $[RuCl_2(\eta^6$-*p*-cymene$)]_2$ (404 mg, 0.66 mmol) in degassed CH_2Cl_2 (10 mL). A solid formed immediately and the reaction mixture was stirred for 4 h in the dark. After filtration through Celite and evaporation of all volatiles, the crude product was purified by column chromatography on silica (CH_3CN/H_2O, 10:1) and recrystallisation from CH_2Cl_2/C_5H_{12} to afford complex **5** as red crystals (155 mg, 27%). ^{1}H NMR ([D$_6$]acetone, 500 MHz, 25 °C): δ = 0.94 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, $NCH_2CH_2CH_3$), 1.29 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H,

CH(CH_3)$_2$], 1.84 (m, 2 H, NCH$_2$CH_2CH$_3$), 1.96 (s, 3 H, C_{cym}–CH$_3$), 2.97 (sept, $^3J_{H,H}$ = 6.9 Hz, 1 H, CHMe$_2$), 4.00 (s, 3 H, NCH_3), 4.32 (br., 2 H, NCH_2CH$_2$CH$_3$) 5.15, 5.47 (2× d, $^3J_{H,H}$ = 5.9 Hz, 2 H, C_{cym}–H), 7.31, 7.37 (2× d, $^3J_{H,H}$ = 2.0 Hz, 2 H, C_{imi}–H) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 125 MHz, 25 °C): δ = 11.8 (NCH$_2$CH$_2$CH_3), 19.2 (C_{cym}-CH_3), 23.2 [CH(CH_3)$_2$], 26.2 (NCH$_2$CH_2CH$_3$), 32.0 (CHMe$_2$), 40.1 (NCH$_3$), 53.9 (NCH_2CH$_2$CH$_3$), 82.6, 88.1 (2× C_{cym}-H), 99.7, 109.6 (2× C_{cym}-C), 122.9, 125.5 (2× C_{imi}-H), 175.9 (C_{imi}-Ru) ppm. HRMS (ES+): calcd. for $C_{17}H_{26}N_2ClRu$ [M – Cl]$^+$ 395.0828; found 395.0837.

Typical Procedure for Catalytic Transfer Hydrogenation: The catalyst (20 μmol) was dissolved in *i*PrOH (10 mL).[28] KOH (0.10 mL of 2 M solution in H_2O, 0.2 mmol) was added and the mixture was heated to reflux for 10 min. The substrate (2.0 mmol), containing the internal standard 3,5-dimethylanisole (0.6 mmol), was then added at once. Aliquots (0.2 mL) were taken at fixed times, quenched with pentane (1 mL) and filtered through a short path of silica. The silica was washed with Et_2O (2× 2 mL) and the combined organic filtrates were analysed by GC–MS or carefully evaporated and analysed by ^{1}H NMR spectroscopy.

Optimised Procedure for Catalytic Transfer Hydrogenation: A 10 mL oven-dried Schlenk-tube was placed under N_2 and charged with *i*PrOH (10 mL). The solvent was degassed by means of three freeze-pump-thaw cycles and placed under N_2 again. The catalyst (20 μmol) was added and dissolved by using ultrasound (10 min, 40 °C). KOH (0.1 mL, 2 M in H_2O, 0.2 mmol) was added and the mixture preheated in a septum-sealed tube at 90 °C for 10 min. Substrate (2.0 mmol) and the internal standard 3,5-dimethylanisole (80 μL, 0.6 mmol) were added with a syringe. Aliquots (0.2 mL) were taken at fixed times and analysed as outlined above.

Supporting Information (see footnote on the first page of this article): Kinetic model including the transformation of **B** directly to **7** and crystallographic details.

Acknowledgments

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absorption corrections applied, μ = 1.191 mm^{-1}. CCDC-810172 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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