Synthesis and properties of a stable, cationic, rhodium Lewis-acid catalyst for hydrosilation, Mukaiyama aldol and cyclopropanation reactions†

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The remarkable stable cationic, three-coordinate, 14-electron rhodium complex 1 has been synthesized, isolated and used as a catalyst for hydrosilation, Mukaiyama aldol and cyclopropanation reactions.

Of the several different catalyst types available for organic reactions, the most diverse are probably the Lewis acids. Ranging from a simple proton to boranes or main group and transition metal complexes, Lewis-acid catalysts now allow for a variety of transformations to be accomplished efficiently and, in many cases, selectively.[1] The requirements for a Lewis-acid catalyst are straightforward: (1) the complex should be electrophilic, and (2) there should be a vacant coordination site. Here, we report the synthesis of the surprisingly stable, cationic, three-coordinate, 14-electron rhodium compound 1.[2] Complexes of 1 with aldehydes and ketones are also described, in addition to preliminary studies employing 1 in catalytic reactions.
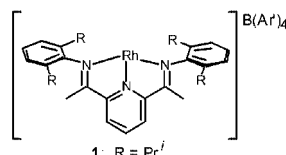
Addition of NaB(Ar′)$_4$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl] to a solution of the rhodium(I) chloride compound 2 in dichloromethane results in quantitative formation of the cationic complex 1 after 1–2 h at room temp., as evidenced by the change in solution color from dark green to orange [eqn. (1)].
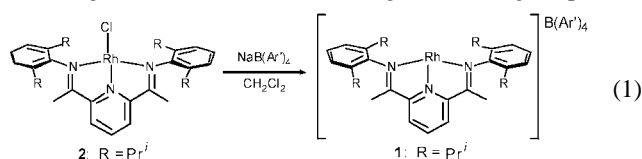
After removing the NaCl by cannula filtration, evaporation of the solvent yields 1 as a stable, dark orange solid which usually contains *ca.* 0.25 equiv. of CH$_2$Cl$_2$, as determined by ^{1}H NMR spectroscopy in d_8-THF. Although 1 can be stored under an inert atmosphere for an indefinite period of time, it is extremely susceptible to hydration, such that it is often more convenient to generate 1 *in situ* immediately prior to use in any subsequent experiments.

The stability of 1 towards the oxidative addition of dichloromethane, a reaction common to rhodium(I) complexes of this type,[3] is of particular significance.[4] Complex 1 was found to be stable in dichloromethane solution indefinitely at room temperature, and even at 40 °C. In addition, 1 can be heated to 70 °C in chlorobenzene without any decomposition. On the other hand, addition of 1 equiv. of methyl iodide to a dichloromethane

solution of 1, generated *in situ* from 2 and NaB(Ar′)$_4$, results in quantitative formation of the rhodium(III) methyl iodide complex 3 after 15–20 min [eqn. (2)]. While we had previously
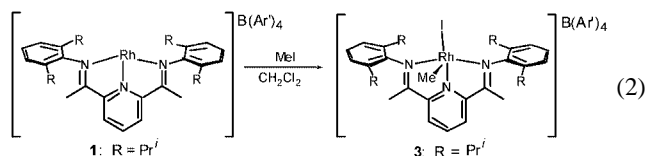
synthesized 3 from the ethylene-bound adduct of 1,[5] this has proven to be a much more simple and convenient route.

The use of chlorinated solvents, whch are very weakly coordinating at best, allows the Lewis-acid characteristics of 1 to be fully exploited. For example, addition of 1 equiv. of either *p*-tolualdehyde or acetophenone to a dichloromethane solution of 1 produces the corresponding adducts 4a and 4b [eqn. (3)], which were isolated as stable solids. From the crystal
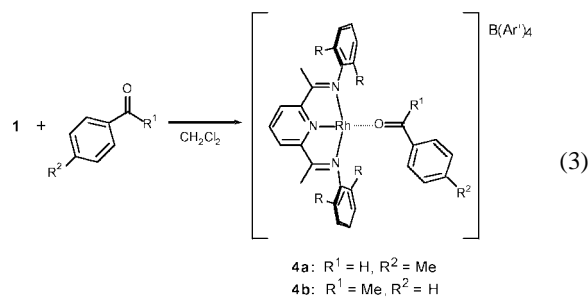
structure of the aldehyde complex 4a (Fig. 1),[6] it can be seen that the aldehyde coordinates in an η^1 fashion. It is also apparent that the imine moieties of the ligand are pulled close to the metal center, such that the attached aryl groups create a 'wedge' in which the aldehyde binds. In fact, when hydrogens are included in the structure, the intramolecular distance of 2.70 Å between the aldehydic hydrogen and the centroid of one of the aryl rings
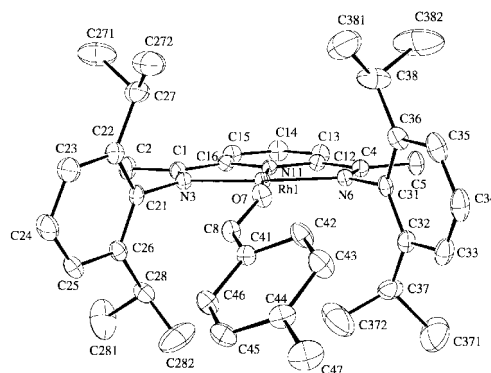

Fig. 1 X-Ray crystal structure of 4a. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Rh(1)–O(7) 2.0728(18), Rh(1)–N(3) 2.0124(23), Rh(1)–N(11) 1.8854(20), O(7)–C(8) 1.227(3); Rh(1)–O(7)–C(8) 129.44(19), O(7)–Rh(1)–N(11) 174.81(9), N(6)–C(4)–C(12) 113.80(25), C(1)–N(3)–C(22) −104.8(6), N(3)–Rh(1)–O(7)–C(8) 41.5(3).

suggests a van der Waals interaction with the aromatic π-cloud. Likewise, the distance of 3.06 Å between the *ortho*-protons on the *p*-tolualdehyde and the other ring indicates a potentially similar interaction. This geometry is verified by the ^{1}H NMR spectrum of **4a**. Resonances for the aldehydic and *ortho* protons appear at 7.45 and 6.68 ppm, respectively, shifted upfield due to the shielding provided by the aryl groups.

When the acetophenone complex **4b** is redissolved in dichloromethane, an equilibrium between the bound and free acetophenone is established. ^{1}H NMR spectroscopy reveals that at room temp., *ca.* 25% of the ketone is not bound to the rhodium center, unlike the aldehyde complex **4a** in which *all* of the aldehyde remains complexed. At lower temperatures, the equilibrium lies further towards complexed acetophenone as expected, and a van't Hoff plot (see ESI†) provides an estimated value of $\Delta H^0 = -16 \pm 2$ kJ mol^{-1} for acetophenone binding.

The availability of complexes **4a** and **4b** led us to screen transformations involving aldehydes and ketones, utilizing **1** as a Lewis acid catalyst. Using 2.5 mol% **1**, the hydrosilation of benzaldehyde and acetophenone with triethylsilane could be effected [eqn. (4)].[1a,7] While the reaction of triethylsilane with
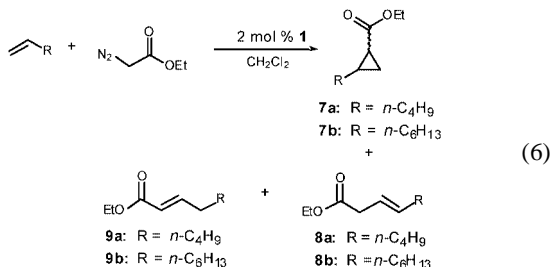
5a: R = H
5b: R = Me

$$(4)$$
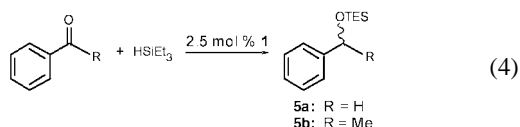
benzaldehyde proceeds to 95% conversion to **5a** after 2 h at 70 °C in chlorobenzene, the reaction with acetophenone to produce **5b** required *ca.* 17 h to reach 90% conversion under similar conditions. Given the lack of reactivity of triethylsilane with **1** and the steric environment imposed by the ligand, it is believed that this reaction in fact proceeds by a Lewis acid-catalyzed mechanism.

The Mukaiyama aldol condensation of a trimethylsilyl enol ether with benzaldehyde can also be catalyzed by **1** [eqn. (5)].[8]

6a: R = H
6b: R = Me

$$(5)$$
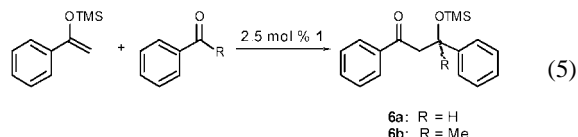
The reaction of benzaldehyde with 1-trimethylsilyloxy-1-phenyl ethylene in chlorobenzene proceeds to 88% conversion to **6a** after heating at 65 °C for 24 h; however, when dichloromethane is used as the solvent, the reaction only proceeds to *ca.* 50% conversion after 24 h at room temperature.

Finally, since carbenes are also two-electron donors, complex **1** seemed to be ideally suited to catalyze cyclopropanation reactions.[9] The reaction of ethyl diazoacetate with α-olefins such as hex-1-ene and oct-1-ene proceeds smoothly; however, carbene insertion into the vinylic C–H bonds was also observed to some extent [eqn. (6)]. Upon monitoring the reaction of

7a: R = *n*-C$_4$H$_9$
7b: R = *n*-C$_6$H$_{13}$

9a: R = *n*-C$_4$H$_9$
9b: R = *n*-C$_6$H$_{13}$

8a: R = *n*-C$_4$H$_9$
8b: R = *n*-C$_6$H$_{13}$

$$(6)$$

hex-1-ene and ethyl diazoacetate by ^{1}H NMR spectroscopy, it was determined that in addition to forming the cyclopropane **7a**, the C–H insertion product **8a** appears initially as well, and slowly isomerizes to the α,β-unsaturated ester **9a** in what is likely a rhodium-catalyzed process. For oct-1-ene, the combined products **7b**, **8b** and **9b** were isolated in 95% yield, and

the product distrubution was determined by ^{1}H NMR to be 85:9:6 respectively.[10]

Surprisingly, these cyclopropanations do *not* proceed using trimethylsilyldiazomethane as a carbene source. Because of the steric limitations imposed by the ligand, incorporation of the TMS group appears to make the diazoalkyl fragment too bulky to coordinate to the rhodium center through the α-carbon, and thus ultimately produce a reactive carbene. In fact, the N-bound adduct of TMS–diazomethane is actually stable enough to be isolated, and we are currently exploring the unique reactivity that results.[11]

In summary, we have demonstrated that **1** is an easily synthesized, isolable compound which shows remarkable stability for a three-coordinate, 14-electron complex. As expected, **1** is a fairly potent Lewis acid, and the steric environment imposed by the ligand creates a binding pocket that must accommodate potential substrates.[12] It is this steric environment, however, which is responsible for the stability of **1** towards oxidative addition reactions common to Rh(ı) complexes—in particular, reaction with chlorinated solvents is suppressed, allowing them to be used as the preferred solvents for synthetic and catalytic applications. In future papers, we will describe the integral role that steric effects play in stabilizing complexes of this type, and report on further studies utilizing **1** as a Lewis acid catalyst.

Notes and references

1 (*a*) *Lewis Acid Reagents: A Practical Approach*, ed. H. Yamamoto, Oxford University Press, New York, 1999; (*b*) *Lewis Acids and Selectivity in Organic Synthesis* ed. M. Santelli and J.-M. Pons, CRC Press, Boca Raton, FL, 1996.

2 A complex employing a similar PNP ligand has been implicated (C. Hahn, M. Spiegler, E. Herdtweck and R. Tabue, *Eur. J. Inorg. Chem.*, 1999, 435), although it was not observed directly and its stability is not evident.

3 H. F. Haarman, J. M. Ernsting, M. Kranenburg, H. Kooijman, N. Veldman, A. L. Spek, P. W. N. M. vanLeeuwen and K. Vrieze, *Organometallics*, 1997, **16**, 887; K. J. Bradd, B. T. Heaton, C. Jacob, J. T. Sampanthar and A. Steiner, *J. Chem. Soc., Dalton Trans.*, 1999, 1109; H. Nishiyama, M. Horihata, T. Hirai, S. Wakamatsu and K. Itoh, *Organometallics*, 1991, **10**, 2706.

4 In a separate study, we have determined that *steric* effects are responsible for the stability of **2** towards the oxidative addition of dichloromethane, and this stability extends to **1** as well. In the series of complexes analogous to **2** where only the *ortho* substituents are varied, we have found that the oxidative addition of dichloromethane occurs when R = H or Me.

5 E. L. Dias, M. Brookhart and P. S. White, *Organometallics*, 2000, **19**, 4995.

6 *Crystal data.* BC$_{73}$F$_{24}$H$_{63}$N$_3$ORh, *M* = 1567.98, triclinic, space group *P*1̄, *a* = 13.3839(6), *b* = 16.3962(7), *c* = 16.8506(7) Å, α = 80.160(1), β = 79.835(1), γ = 86.890(1)°, *U* = 3585.1(3) Å^3, *Z* = 2, μ(Mo-Kα) = 0.35 mm^{-1}, 45 784 reflections measured, 17 165 unique (*R*$_{int}$ = 0.018) which were used in all calculations. The final *wR*(*F*^{2}) was 0.056 (all data). CCDC 182/1892. See http://www.rsc.org/suppdata/cc/b0/b007815h/ for crystallographic files in .cif format.

7 For examples of Lewis-acid catalyzed hydrosilation, see; D. J. Parks, J. M. Blackwell and W. M. Piers, *J. Org. Chem.*, 2000, **65**, 3090; D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440; Y. S. Song, B. R. Yoo, G. H. Lee and I. N. Jung, *Organometallics*, 1999, **18**, 3109.

8 See: T. Mukaiyama, *Org. React.*, 1982, **28**, 203 and references therein.

9 For reviews of transition metal-catalyzed cyclopropanations, see: M. P. Doyle and D. C. Forbes, *Chem. Rev.*, 1998, **98**, 911; M. P. Doyle, *Acc.Chem. Res.*, 1986, **19**, 348; G. Maas, *Top. Curr. Chem.*, 1987, **137**, 75.

10 It was observed in NMR experiments that the product distribution does not change over the course of these reactions, indicating that the products **8** and **9** are not formed by acid-assisted opening of the cyclopropanes **7**.

11 E. L. Dias, M. Brookhart and P. S. White, *J. Am. Chem. Soc.*, in press.

12 For a recent review of Lewis-acid catalysts with designed binding pockets, see: H. Yamamoto and S. Saito, *Pure Appl. Chem.*, 199, **71**, 239 and references therein.