

Preliminary Communications

Novel organomanganese(II) complexes active as homogeneous catalysts in manganese(II)/copper(I) catalyzed carbon-carbon bond formation reactions.

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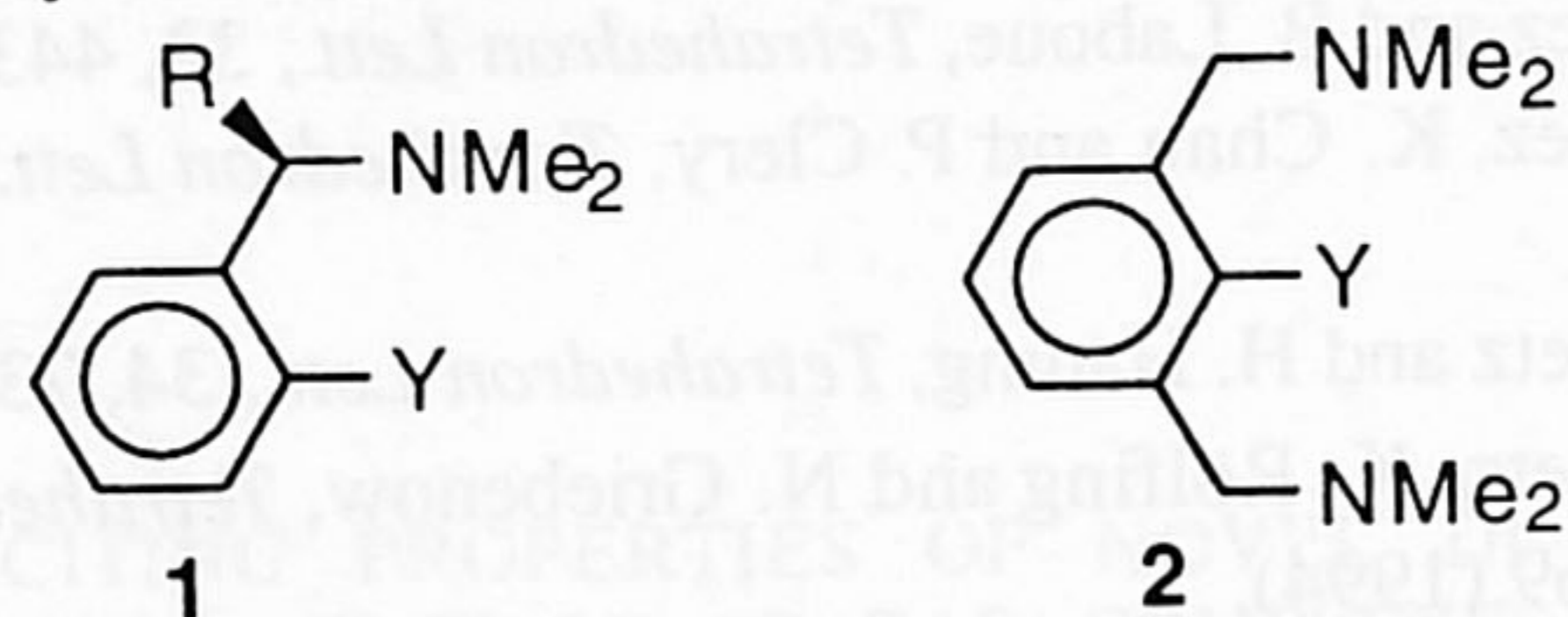
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Abstract: Novel organomanganese complexes **3** and **4** were prepared *via* transmetalation of the corresponding organolithium reagent. These new complexes are active catalysts in manganese/copper mediated cross-coupling reactions.

We have shown that arylamine **1**, and aryldiamine **2**, where Y can be a variety of groups including H, can be employed in organometallic complexes that are active in homogeneous catalysis.

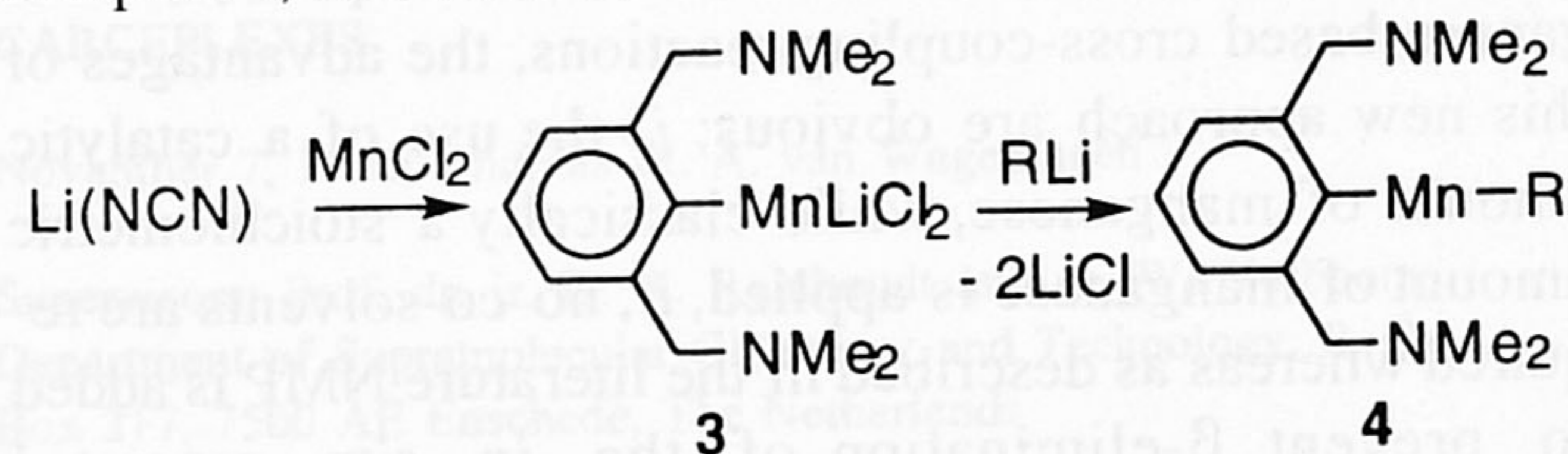


Examples of such applications in catalysis are: *i*, in copper catalyzed enantioselective conjugate addition reactions (**1**, R = Me, Y = SCu)¹, *ii*, in enantioselective 1,2-additions of R₂Zn to aldehydes (**1**, R = Me, Y = SZnEt)², *iii*, in ring-opening metathesis polymerization (**1**, R = H, Y = W(R') (=NPh) (=CHSiMe₃)³, *iv*, in Kharasch addition reactions of haloalkanes to olefins (**2**, Y = NiX)⁴, and *v*, in hydrogenation and hydrogen transfer reactions (**2**, Y = RuCl(PPh₃)⁵.

We now report our first results on the application of manganese based complexes **2** (Y = MnX or MnR) in catalyzed C-C bond formation reactions.

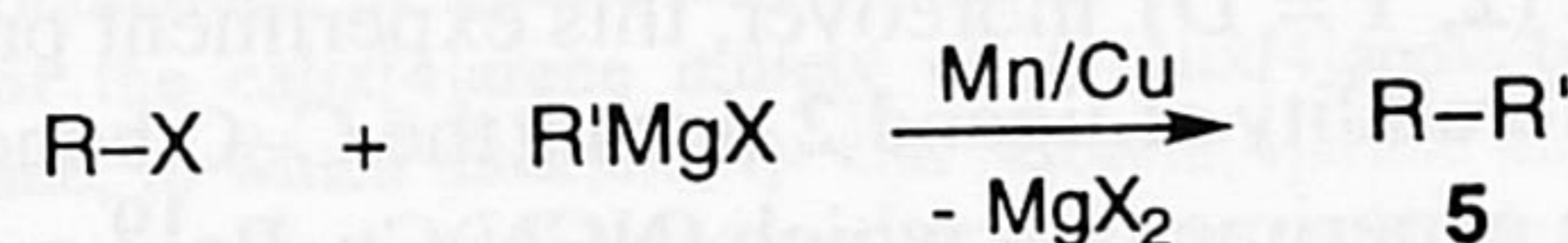
In recent years a growing interest exists in the organometallic and coordination chemistry of manganese complexes due to the role of this metal in, *e.g.*, catalytic oxidation chemistry⁶ or manganese mediated organic reactions⁷⁻¹³. Of the latter especially the *in situ* preparation of organomanganese(II) species by reaction of a manganese(II) salt with a Grignard or organolithium reagent has found wide application⁷⁻⁹. However these manganese(II) salt based systems lack the possibility of tuning for example the stereochemical outcome of the reaction. This disadvantage can be overcome by introduction of a modifiable non-transferable ligand based on **1** or **2**.

Reaction of the lithium derivative of **2**, (Y = Li and [C₆H₃(CH₂NMe₂)_{2-2,6}] abbreviated as NCN) with one equivalent of MnCl₂ afforded a yellow-green, paramagnetic solid for which the elemental analysis pointed to the stoichiometry LiMnCl₂(NCN), **3**¹⁴. Reaction of **3** with one equivalent of an organolithium reagent RLi (R = Me, Bu, Ph) afforded after work-up a dark green paramagnetic oil, tentatively assigned as a heteroleptic diorganomanganese complex **4**, free of LiCl.



Due to the paramagnetic character of **3** and **4** structural characterization by NMR techniques is hampered¹⁵, but reaction of both **3** and **4** with D₂O afforded exclusively the 2-deuterio derivative of **2** (Y = D) as was evidenced by ¹H and ¹³C NMR spectroscopy and mass spectroscopy. This indicates that in **3** and **4** prior to reaction with D₂O a metal to carbon bond was present.

The new organomanganese species **3** and **4**, either as pure compounds or *in situ* prepared (**3**) were tested as catalysts in the cross-coupling reaction of Grignard reagents with organyl bromides as well as in 1,4-addition reactions of Grignard reagents to α,β-unsaturated ketones.



Under optimized reaction conditions¹⁶ **3** was found to be an excellent catalyst in the manganese/copper mediated cross-coupling reaction of alkyl bromides and Grignard reagents *cf.* Table I.

Table I Product yields of R–R' 5 obtained from cross-coupling reactions of Grignard reagents with alkyl bromides.

entry	alkyl bromide	Grignard reagent	Yield (%)
1	<i>n</i> -C ₈ H ₁₇ Br	<i>n</i> -BuMgCl	83
2	<i>n</i> -C ₈ H ₁₇ Br	<i>i</i> -PrMgCl	75
3	<i>n</i> -C ₈ H ₁₇ Br	<i>t</i> -BuMgCl	84
4	<i>n</i> -C ₈ H ₁₇ Br	<i>s</i> -BuMgCl	92
5	C ₄ H ₉ CO(CH ₂) ₁₀ Br	<i>n</i> -BuMgCl	91
6	C ₂ H ₅ OC(O)(CH ₂) ₂ Br	<i>n</i> -BuMgCl	89
7	CH ₂ =CH(CH ₂) ₂ Br	<i>n</i> -C ₁₄ H ₂₉ MgCl	91
8	TMSC≡C(CH ₂) ₂ Br	<i>n</i> -C ₁₄ H ₂₉ MgCl	89

During these reactions the formation of complex 4 is very likely. The reaction of *n*-C₈H₁₇Br with *n*-BuMgCl (entry 1 in Table I) was carried out using pure 3, pure 4 and *in situ* prepared 3, *i.e.* addition of one equivalent of Li(NCN) (2, Y = Li) to MnCl₂ prior to the addition of substrate and Grignard reagent. Since the chemoselectivity and yield of these reactions are essentially the same, further catalytic experiments were carried out with *in situ* prepared 3.

The cross-coupled products are formed with excellent chemoselectivity and high yields irrespective of the type of Grignard reagent (primary, secondary, tertiary) that is used, *cf.* entries 1–4 in Table I. Especially the reaction with secondary Grignard reagents, *cf.* entry 2, is notable. Yields of cross-coupled products obtained via the classical Li₂CuCl₄ reagent do not exceed 24 %¹⁷. The presence of unsaturated groups (entries 7 and 8) or heteroatom functionalities (entries 5 and 6), of which especially the substrate susceptible towards β-elimination is of interest (entry 6), does not influence either the selectivity or the yield of cross-coupled product (traces of olefins or rearrangement products could not be detected)¹⁶.

Although, the yields and selectivities of the obtained cross-coupled products using our newly developed method are comparable to those reported for classical cuprate or manganese based cross-coupling reactions, the advantages of this new approach are obvious; *i*, the use of a catalytic amount of manganese, while classically a stoichiometric amount of manganese is applied, *ii*, no co-solvents are required whereas as described in the literature NMP is added to prevent β-elimination of the *in situ* generated organomanganese species¹⁸, and *iii*, reaction times are short, typically less than one hour, *versus* several hours in the literature methods.

Mechanistically not very much is yet known about the manganese/copper mediated reactions. That copper plays a crucial role became clear from an experiment in which no CuCl was added prior to addition of the substrate and the Grignard reagent. From this reaction no cross-coupled product was obtained. That organometallic species are present during the reaction became evident when the reaction mixture was quenched with D₂O. After acidic work-up of the aqueous phase all 2 was recovered as its monodeuterio derivative (2, Y = D). moreover, this experiment proves the non-transferability of ligand 2 during the C–C bond formation. In an experiment in which (NCN)Cu₂Br¹⁹ was added instead of CuCl while MnCl₂ was omitted only minor amounts of cross-coupled products were obtained, indicating that it is not a simple transmetallation reaction of an

NCN group from manganese to copper that occurs. Most likely there is a subtle cooperative effect of copper and manganese resulting in the selective formation of cross-coupled products in high yield.

Preliminary experiments have shown that 3 and 4 are also active in the manganese/copper mediated 1,4-addition of Grignards to α,β-unsaturated ketones. Moreover, it has been found that an enantiopure chiral modification of 3 and 4 (substituted at the benzylic positions) induces enantioselectivity in both C–C bond formation reactions. These topics are currently under investigation.

Acknowledgement

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- Anal. calcd. for 3, C₁₂H₁₉Cl₂LiMnN₂: C, 44.47; H, 5.91; N, 8.64; found C, 44.40; H, 6.05; N, 8.66.
- Structural characterization of the novel organomanganese compounds by ESR and magnetic measurements will be the subject of a forthcoming study.
- To a suspension of 1 mmol MnCl₂ in 25 mL of THF was added 1 mmol (NCN)Li dissolved in 5 mL of THF. The reaction mixture was stirred until a clear solution was obtained. To this solution 0.5 mmol CuCl was added and the mixture was cooled to 5 °C. Subsequently 10 mmol of the corresponding bromide and 10 mmol of the Grignard were added. The reaction mixture was stirred for an additional 15 min. at 5 °C and hydrolyzed with 50 mL 4M HCl. After work-up (pentane extraction and flash distillation) the products were isolated as colourless liquids; isolated yields of pure products are given in Table I. The products were identified by comparison of their GC, MS and NMR data with those of authentic samples.
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- Most probably the two potentially coordinating amino substituents in 3 and 4 have a similar stabilizing effect.
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