Coupling of alkynols and a phenyl group to a novel η^5-dihydronaphthalenide ligand on a ruthenium template†

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We report the highly selective assembly of unprecedented η^5-1-methylene-1,2-dihydronaphthalenide ligands from the stoichiometric coupling of a phenyl group and two equivalents of disubstituted propargylic alcohols; in this reaction, tetraphenylborate acts as a phenylating agent.

The coupling of alkynes is of pivotal importance for the assembly of a broad variety of unsaturated cyclic and linear molecules. Typical examples include their cyclotrimerization to substituted arenes[1,2] and their linear coupling to butenynes, butatrienes, hexadienynes or octatetraenes.[3–7] Amongst the wealth of such coupling reactions efficient transformations of propargylic alcohols are extremely rare. This is because the free hydroxy group strongly interacts with many of the cyclisation catalysts employed to date, thus preventing efficient transformations. The few reported examples include their linear tail-to-tail dimerization to give hydroxy substituted butadienones,[8] their cyclodimerization to alkylidene cyclobutenes in the presence of a carboxylic acid[9] and the insertion of alkynols into a ruthenacyclopentatriene to give vinylbutatrienyl ligands.[10] The cyclotrimerization of 2-methylbut-3-yn-2-ol to either 1,2,4- or 1,3,5-$C_6H_3(CMe_2OH)_3$[11,12] and the cyclotrimerization of but-2-yne-1,4-diol to the corresponding benzene have also been observed.[13]

We report here on the co-cyclisation of two equivalents of disubstituted propargylic alcohols and a phenyl group to afford unprecedented η^5-1-methylene-1,2-dihydronaphthalen-2-ide ligands with tetraphenylborate as a phenylating agent. We discovered this unusual coupling reaction during our investigations on catalytic transformations of propargylic alcohols with ruthenium complexes such as $[(p\text{-cymene})RuCl_2]_2$, **1**. Treatment of **1** with $NaSbF_6$ and an excess of 2-methylbut-3-yn-2-ol gave only the known trichloro bridged dimer $[\{(p\text{-cymene})Ru\}_2(\mu\text{-Cl})_3]^+$ SbF_6^- which was characterized by NMR spectroscopy and X-ray analysis. When other halide abstracting agents were employed, intractable product mixtures were obtained. In the presence of tetraphenylborate, however, a single clean product **2a** was formed as was indicated by NMR spectroscopy.

Since all our attempts to grow X-ray quality crystals of this product have failed up to now, its identification rests on the results from NMR spectroscopy (1D and 2D NMR), IR, mass spectrometry and analytical data.‡ The ^1H and $^{13}C\{^1H\}$ NMR spectra display the resonances of an intact BPh_4^- counterion and a π-conjugated *p*-cymene ligand that are present in a 1 : 1 ratio. The appearance of four distinguishable sets of π-coordinated CH-units and anisochronic methyl groups in the isopropyl substituent of the cymene unit indicates that the plane of symmetry through this ligand has been lost. The observation of four additional methyl signals suggests that two equivalents of the propargylic alcohol have been incorporated into the product. The single OH proton signal (δ = 1.78) in the ^1H NMR and strong bands at 3545 cm^{-1} and 1175 cm^{-1} arising from the OH and out-of-phase-C–C–O stretches in the IR spectrum are characteristic of a tertiary alcohol. The presence of just one OH group in the product suggests that one equivalent of water was lost. The remaining ^1H and ^{13}C resonances comprise the signals of four quaternary carbon atoms and two more olefinic CH-units that resonate at rather high field. These are attributable to ruthenium coordinated =CH moieties. Four additional =CH-signals are partially overlapped by the resonances of the counterion and are characteristic of non-coordinated arenes.

The two-dimensional C,H and H,H correlation spectra allowed us to establish the ligand structure as it is depicted in Chart 1. Two methyls and the OH group are bonded to an aliphatic carbon atom which resonates at 70.0 ppm. The two remaining methyl groups and two quaternary olefinic carbon atoms ($\delta(^{13}C)$ = 121.5, 123.0) form a C=CMe_2 fragment that presumably originates from the incorporation of a second propargylic alcohol with concomitant loss of one equivalent of water. The analysis of further one-bond and long-range correlations in H,C HSQC and HMBC spectra suggests that the terminal carbon atom of the isobutylidene unit, two π-coordinated CH carbon units ($\delta(^{13}C)$ = 48.5, 77.4), and the three remaining quaternary carbon atoms form a six-membered ring. One of the latter ($\delta(^{13}C)$ = 113.8) is substituted by the CMe_2OH group while the two remaining ones ($\delta(^{13}C)$ = 81.7, 101.4) and the four residual =CH-units comprise a second

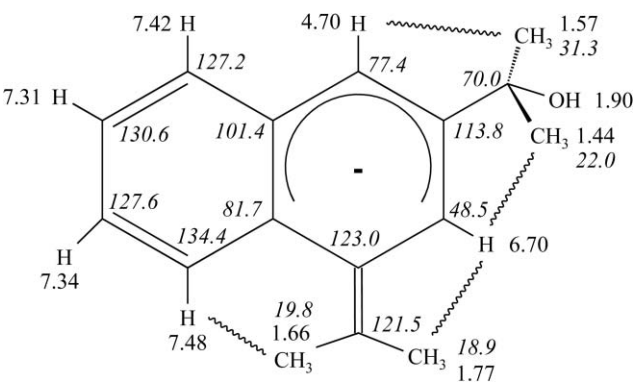

Chart 1 ^1H and ^{13}C shifts (in italics) of the η^5-dihydronaphthalenide ligand of **2a**; observed NOEs are indicated as wavy lines.

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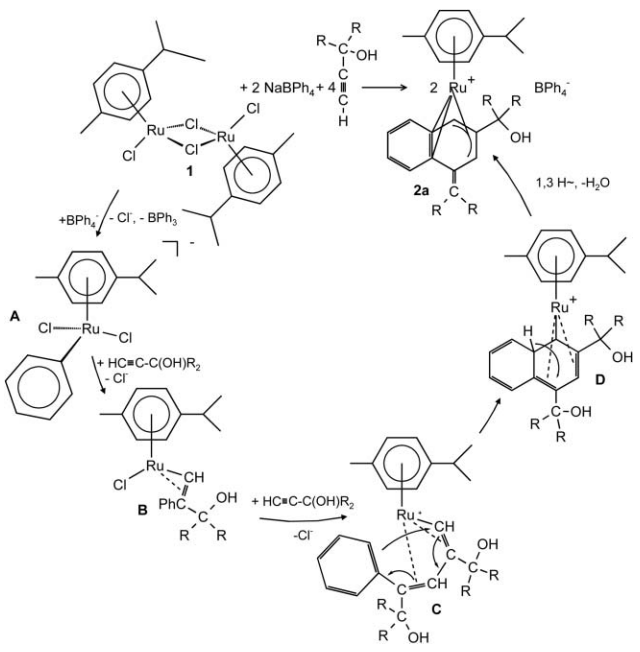
six-membered ring that is annellated with the first one to give a naphthalene skeleton (see Chart 1). The positions and spatial arrangement of the exocyclic propylidene and CMe_2OH moieties were substantiated by the detection of NOE correlations between the CH proton at 4.70 ppm and the methyl protons at 1.57 ppm, the CH proton at 6.70 ppm and the CH_3 protons at 1.44 and 1.77 ppm, and between one of the aromatic protons at 7.48 ppm and the nuclei of the second isopropylidene CH_3 group at 1.66 ppm. The observation of characteristic upfield shifts for five of the six atoms in the disubstituted ring (*cf.* Chart 1) suggests that the naphthalene framework is bonded in an η^5-coordination mode and, since all carbon atoms in the fused ring system and the exocyclic methylene unit are three-coordinate, carries a negative charge. The whole complex cation may thus be described in terms of a Ru(II) atom that is coordinated by a neutral η^6-bound cymene and a uninegative benzannellated 1-methylene-1,2-dihydrocyclohexadienide ligand which behaves essentially as a pentadienyl equivalent. Positive ion EI (70 eV) and CI MS spectra (NH_3 reactand gas) gave the molecular ion peak at *m/z* 462.1 in 88% intensity with the correct isotope pattern (see Supporting Information). The base peak at *m/z* 444.1 results from the loss of water from the CMe_2OH entity.

As to the formation of the dihydronaphthalenide ligand we suggest the reaction sequence outlined in Scheme 1. In the first step $NaBPh_4$ acts as a phenylating agent toward the *p*-cymene ruthenium dimer, giving $[(p\text{-cymene})RuCl_2(Ph)]^-$. Substitution of one chloride by one equivalent of the propargylic alcohol would then render $[(p\text{-cymene})RuCl(Ph)(\eta^2\text{-HCCCMe}_2OH)]$. Migratory insertion of the alkyne into the Ru–phenyl bond, possibly *via* the corresponding vinylidene $[(p\text{-cymene})Cl(Ph)Ru{=}C{=}CHCMe_2OH]$, would give the unsaturated vinyl intermediate **B**. Coordination of one further equivalent of the alkynol followed by another insertion step would then give the 4-phenylpentadienyl intermediate **C**. Electrocyclic ring closure would generate intermediate **D** which transforms into the final product *via* a 1,3 hydrogen shift with concomitant aromatization followed by dehydration. While all intermediates along the proposed reaction path are speculative, we could show that the uncoordinated phenyl ring of the naphthalenide skeleton as well as the hydrogen atom lost in the dehydration step both arise from the BPh_4^- anion.[14] When BPh_4^--d_{20}[15] was employed, all of the CH resonances of the non coordinated part of the naphthalenide ring appeared as non-binomial quartets in ^{13}C NMR spectra and none of the corresponding proton resonance signals could be observed. Likewise, the OH signal at 1.78 ppm and the IR OH band at 3545 cm^{-1} were considerably weakened, and the latter is partially replaced by a sharp intense band at 2242 cm^{-1}. This points to partial H/D exchange with the water liberated as DOH in the dehydration process. In the EI MS the molecular ion peak shifts by five mass units, attesting to the incorporation of five D atoms.



Scheme 1 Proposed reaction sequence in the formation of complexes **2**.

We note that action of the BPh_4^- anion as a phenylating agent, although rare, is not without precedent, especially in ruthenium chemistry. Thus, $[\{CpRu(CO)_2\}_2(\mu\text{-X})]^+$ (X = Cl, Br) reacts with $NaBPh_4$ to give a mixture of $[CpRu(CO)_2X]$ and $[CpRu(CO)_2(Ph)]$.[16] Any of the other reaction steps in Scheme 1 are elementary processes in many transition metal catalyzed or mediated conversions of alkynes. We also note the high regioselectivity observed in each of the addition/insertion steps. In fact, we have not been able to detect any other regioisomer of **2a** in the crude product by NMR spectroscopy.

In order to widen the scope of this reaction we also examined other alkynols. Essentially the same results were obtained for 1-ethynylcyclohexanol and 1-ethynylcyclopentanol, giving complexes **2b,c** (see Supporting Information)†. 2-Phenylbutynol and 1,1-diphenyl-2-propyn-1-ol, on the other hand, gave a complex mixture from which no clean products could be obtained or identified. 1,1-Dimethylpropyne also failed to react. The related dimer $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ gave only small amounts of a complex corresponding to **2a** when treated with $NaBPh_4$ and 2-methylbut-3-yn-2-ol either at room temperature or under reflux conditions. We then considered that electrophilic addition to the negatively charged site(s) of the coordinated naphthalenide ring might induce a haptotropic rearrangement to a symmetrical dicationic sandwich structure where the ruthenium atom is coordinated to the benzene ring of the dihydronaphthalenide ligand. Treatment of **2a** with various electrophiles such as MeI, Meerwein's salt OMe_3^+ BF_4^-, CF_3SO_3Me, HBF_4 and CF_3SO_3H however resulted in no detectable changes of the cation's NMR signals even after prolonged reaction times. This attests to the low electrophilicity of the coordinated dienide ring.

In summary, we have disclosed a novel co-cyclization of a phenyl group and 2 equivalents of an alkynol to an unprecedented 2-methylene-2,3-dihydronaphthalenide ligand which acts as a Cp^- equivalent. The uncoordinated phenyl ring originates from the BPh_4^- counterion as has been shown by deuterium labeling. This establishes a further example of this anion acting as a phenylating agent.

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Notes and references

‡ Selected spectroscopic data: compound **2a**: ^{1}H-NMR (250 MHz, CD_2Cl_2), δ 1.28, 1.41 [each 3H, d, $CH_3(^{i}Pr)$, $^{3}J_{H-H}$ = 6.88 Hz], 1.44, 1.57 [each 3H, s, $C(CH_3)_2OH$], 1.66, 1.77 [each 3H, s, CH_3(naph)], 1.78 [1H, s(br.), OH], 2.05 [3H, s, CH_3(cym)], 2.65 [1H, hept, CH (^{i}Pr), $^{3}J_{H-H}$ = 6.88 Hz], 4.18 [1H, d, CH(cym), $^{3}J_{H-H}$ = 6.2 Hz], 4.7 [1H, s, CH(naph)], 4.82, 5.31, 5.36 [each 1H, d, CH(cym), $^{3}J_{H-H}$ = 6.2 Hz], 6.7 [1H, s, CH(naph)], 7.31 [1H, t, $^{3}J_{HH}$ = 7.12 Hz, CH(naph)], 7.34 [1H, t, CH(naph), $^{3}J_{H-H}$ = 7.18 Hz], 7.42 [1H, t, CH(naph)], 7.48 [1H, m, CH(naph)]. ^{13}C-NMR (250 MHz, CD_2Cl_2), δ 18.9, 19.8 [each s, CH_3(naph)], 19.2 [s, CH_3(cym)], 21.95, 31.3 [each s, $C(CH_3)_2OH$], 24.2, 31.8 [s, $CH_3(^{i}Pr)$], 33.85 [s, $CH(^{i}Pr)$], 48.5 [s, CH(naph)], 70.0 [s, CMe_2OH], 77.4 [s, CH(naph)], 81.7 [s, C_q(naph)], 84.7, 88.2, 86.7, 90.6 [each s, CH(cym)], 101.4 [s, C_q(naph)], 105.6, 116.2 [each s, C_q(cym)], 121.5, 123.0 [each s, C=C(naph)], 127.2, 127.6, 130.6, 134.4 [each s, CH(naph)]. IR (KBr) 3545 (OH), 1596 (C=C), 1175 (CCO). CH analysis for $C_{50}H_{53}BORu$: calculated (measured): C 76.81 (75.78), H 6.83 (6.61). MS: positive ion EI, 70 eV, 470 K: 462.1 (M^+, 13%), 444.1 ($M^+ - H_2O$, 31%); positive ion CI, 400 K: 462.1 (M^+, 88%), 444.1 ($M^+ - H_2O$, 100%).

1 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, in *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, 1987.

2 S. Saito and Y. Yamamoto, *Chem. Rev.*, 2000, 2901.

3 C. Slugovc, D. Doberer, C. Gemel, R. Schmid, K. Kirchner, B. Winkler and F. Stelzer, *Monatsh. Chem.*, 1998, **129**, 221.

4 C. S. Yi and N. Liu, *Synlett*, 1999, 281.

5 H. Werner, M. Schäfer, J. Wolf, K. Peters and H. G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 191.

6 M. A. Esteruelas, J. Herrero, A. M. López and M. Oliván, *Organometallics*, 2001, **20**, 3202.

7 C. S. Chin, H. Lee, H. Park and M. Kim, *Organometallics*, 2002, **21**, 3889.

8 B. M. Trost and M. T. Rudd, *J. Am. Chem. Soc.*, 2001, **123**, 8862.

9 J. Le Paih, S. Derién, C. Bruneau, B. Demerseman, L. Toupet and P. H. Dixneuf, *Angew. Chem.*, 2001, **113**, 2996.

10 E. Becker, K. Mereiter, M. Puchberger, R. Schmid and K. Kirchner, *Organometallics*, 2003, **22**, 2124.

11 M. V. Russo and A. Furlani, *Tetrahedron Lett.*, 1976, **30**, 2655.

12 P. Bicev, A. Furlani and G. Sartori, *Gazz. Chim. Ital.*, 1973, **103**, 849.

13 M. S. Sigman, A. W. Fatland and B. E. Eaton, *J. Am. Chem. Soc.*, 1998, **120**, 5130.

14 The BPh_3 released in this reaction is further converted to triphenylboroxine, methanol and benzene as is indicated by NMR and MS data.

15 J. D. Wilkey and G. B. Schuster, *J. Org. Chem.*, 1987, **52**, 2117.

16 R. J. Haines and A. L. du Preez, *J. Am. Chem. Soc.*, 1971, **93**, 2820.