Heterobimetallic Coinage Metal-Ruthenium Complexes Supported by Anionic N-Heterocyclic Carbenes

Sebastian Planer,[b] Jenni Frosch,[a] Marvin Koneczny,[b] Damian Trzybiński,[b] Krzysztof Woźniak,[b] Karol Grela,*[b] and Matthias Tamm*[a]

Abstract: The lithium complexes [(WCA-NHC)Li(toluene)] of anionic N-heterocyclic carbenes with a weakly coordinating borate moiety (WCA-NHC, WCA = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidine) were used for the preparation of silver(I) or copper(I) WCA-NHC complexes. While the reactions in THF with AgCl or CuCl afforded anionic mono- and dicarbenes complexes with solvated lithium counterions [Li(THF)₃]⁻ (n = 3, 4), the reactions in toluene proceeded with elimination of LiCl and formation of the neutral phosphate and arene complexes [(WCA-NHC)M(PPh₃)] and [(WCA-NHC)M(toluene)] (M = Ag, Cu). The latter were used for the preparation of chlorido- and iodido-bridged heterobimetallic Ag/Ru and Cu/Ru complexes [(WCA-NHC)M(μ-X)₂Ru(PPh₃)](η²-p-cymene)] (M = Ag, Cu; X = Cl, M = Ag, X = I). Surprisingly, these complexes resisted the elimination of CuCl, AgCl, or AgI, precluding WCA-NHC transmetalation.

Introduction

Anionic derivatives of N-heterocyclic carbenes (NHCs) have become an important subclass of these ubiquitous and indispensable carbon-donor ligands,[1] with C–H metatation and backbone functionalization of imidazolin-2-ylidene systems being arguably the most important strategy for the preparation of ditopic carbenes of type I (Figure 1).[2] For example, with X = BEt₃, AlMe₃, CO₂, ZnR₂ (R = Et, Bu), M(N(SiMe₃))₂ (M = Zn, Ge, Sn, Pb).[3] Accordingly, most of these species were isolated as lithium salts by deprotonation of 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidine (IDipp) with n-Buli, followed by treatment of the intermediate “viable anionic N-heterocyclic dicarbene”[4] with the respective electrophile. Thus, addition of fluoroboranes afforded so-called WCA-NHC systems with a weakly coordinating anionic borate unit. The resulting solvated lithium salts [(WCA-NHC)Li(solvent)] (1) were used as transmetalation reagents for the preparation of late transition metal complexes, for example, AuI,[5] RhI,[6] IrI,[7] Au(II),[8] Ir(II),[9] which were preferably used as homogeneous catalysts for applications in nonpolar solvents. Early transition metal cyclopentadienyl-titanium(IV) and imido-vanadium(V) complexes were also prepared and used as pre-catalysts for ethylene copolymerization.[12] Related anionic analogues of NHCs in which the borate unit is attached to the heterocycle via a methylene (CH₂) spacer were also used in transition metal chemistry.[13] Lately, the lithium salts 1 were employed for the preparation of WCA-NHC complexes of the heavier p-block elements, covering groups 13,[14] 15,[15] 16,[16] and 17.[17]

In search for alternative transmetalation reagents, sodium and potassium salts of WCA-NHCs were recently introduced, however, their synthesis through deprotonation of IDipp with...
Schlosser base combinations of sodium or potassium bis-(trimethylsilyl)lamides and n-BuLi leaves room for further optimisation.\textsuperscript{18} Therefore, we turned our attention to WCA-NHC complexes of the lighter coinage metals, since silver(I) and as well as copper(I) NHC complexes have become well-established and widely used carbene transfer reagents.\textsuperscript{19} As a result, we present, among other things, the synthesis and characterization of Ag(I) and Cu(I) complexes such as \([\text{WCA-NHC}M(\eta^2\text{-toluene})]\) (5, \(M = \text{Ag, Cu}\)) and their attempted use for the preparation of ruthenium(II) WCA-NHC complexes (Figure 1). To our surprise, however, it was found that the anticipated transmetalation reactions do not proceed with the elimination and precipitation of silver(I) or copper(I) halides but can be used for the controlled assembly of heterobimetallic Ag/Ru and Cu/Ru complexes.

Results and Discussion

We first studied the reaction of the lithium carbene complex 1-toluene with one equivalent of silver(I) and copper(I) chloride in THF solution, which afforded the ionic complexes 2-THF and 3 after filtration through Celite\textsuperscript{a} and recrystallization from THF/n-hexane solution (Scheme 1). Regardless of the 1:1 stoichiometry, the reaction with AgCl proceeded with formation of the anionic dicarbene silver complex with a linear C–Ag–C angle of 178.08(10)° and Ag–C bond lengths of 2.141(3) and 2.151(3) Å, which is reminiscent of the structural parameters repeatedly established for the cationic analogues \([\text{(IDipp)}_2\text{Ag}]^+\)\textsuperscript{20} and \([\text{(IMes)}_2\text{Ag}]^+\)\textsuperscript{21} (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene). The lithium counterion is solvated by four THF molecules and resides in a slightly distorted tetrahedral environment (Figure 2). It is interesting to note that the $^{13}\text{C}$ NMR spectrum exhibits a nicely resolved doublet of doublets at 183.9 ppm, with coupling constants $^1J_{\text{C,Ag}}$ of 195 and 224 Hz for $C_{\text{carbene}}$ bonding to the $^{107}\text{Ag}$ and $^{109}\text{Ag}$ nuclei. These values fall in the range observed for other homoleptic silver(I)-dicarbene complexes,\textsuperscript{19a,22} for example, $\delta = 183.6$ ppm, $^1J_{\text{C,Ag}} = 188/209$ Hz for \([\text{(IMes)}_2\text{Ag}]\text{[CF}_3\text{SO}_3\text{]}\)\textsuperscript{21a}

The copper complex 3 crystallized with two independent molecular anions \([\text{WCA-NHC}Cl]^-\) in the asymmetric unit, together with one \([\text{Li(THF)}_3]^+\) and another \([\text{Li(THF)}_4]^+\) unit that interacts with one of the chlorido ligands (Figure 3). The copper atoms have linear coordination spheres with $C_1$–Cu1–Cl1 =

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\includegraphics{Scheme_1.png}
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\textbf{Scheme 1.} Synthesis of silver(I) and copper(I) WCA-NHC complexes in THF solution.
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Che rnal and C58–Cu–Cl2 = 179.18(10)°, and the copper-carbon bond lengths of 1.877(3) Å (Cu1–C1) and 1.879(3) Å (Cu2–C58) are in the same but slightly shorter range compared to the neutral analogues [(dipp)AgCl][25] and [(mes)CuCl][26].

Related copper(I) chloride complexes bearing anionic malonate or enolate functionalized anionic N-heterocyclic carbenes have also been reported.[27,28] It should be noted that we also obtained crystals of the complex [Li(THF)]2[(WCA-NHC)Cu2(μ-Cl)], in which the chlorido ligand is bridging two (WCA-NHC)Cu moieties; see Figure S11 in the Supporting Information for a presentation of the crystal structure. These findings prompted us to question our synthetic strategy, since carrying out the reactions in THF solution prevented the formation and precipitation of lithium chloride by solvation and resulted in ionic complexes of various, somewhat unreliable compositions. Moreover, transmetalation reactions consistently failed with 2 and 3, and for instance, the reaction of 3 with [(η⁴-p-cymene)RuCl3]2 afforded a bimetallic salt consisting of the non-interacting complex ions [(η⁴-p-cymene)Ru(μ-Cl)]⁺ and [(WCA-NHC)CuCl]⁻ (see the Supporting Information, Figure S10).

Therefore, we turned our attention to WCA-NHC transfer reactions in toluene solution, and initial experiments of 1 in toluene and addition of [(Ph3P)MCl] afforded the complexes [(WCA-NHC)M(Ph3P)] (4) as colorless (4a: M = Ag) and yellow (4b: M = Cu) crystalline solids in 69% and 63% yield, respectively, after stirring for ca. 2 h, filtration through Celite® and recrystallization from dichloromethane/n-hexane or THF/n-hexane solutions (Scheme 2). The NMR spectroscopic characteristics are similar to those previously established for the corresponding gold(I) complex [(WCA-NHC)Au(Ph3P)], however, the 31P NMR resonances are found at significantly higher field, i.e., at 18.3 ppm (4a) and 8.6 ppm (4b) in comparison with 40.5 ppm reported for the gold congener.[29]

For the silver complex 4a, this signal is observed as a doublet of doublets with 1JAg = 462/333 Hz for phosphorus coupling with the 109Ag/109Ag nuclei. In contrast, the 13C NMR signal for the carbene carbon atom in 4a could not be resolved, whereas 4b gave rise to doublet at 177.2 ppm with 1JCu = 69 Hz.

The complexes 4 were further characterized by single-crystal X-ray diffraction analysis; they are isotypic and crystallize in the monoclinic space group P2₁/n. The molecular structure of the silver complex 4a is shown in Figure 4, whereas the molecular structure of the copper complex 4b is presented in the Supporting Information (Figure S4). Selected bond lengths and angles are summarized in Table 1. The two-coordinate Ag and Cu atoms display distorted linear environments with C1–M–P1 angles of 166.81(6)° (4a) and 166.23(4)° (4b). The metal-carbon and metal-phosphorus bond lengths of 2.085(2)/2.343(4) Å (Ag1–C1/Ag1–P1) and 1.9063(12)/2.1926(4) Å (Cu1–C1/Cu1–P1) fall in the expected ranges and are similar to those established for cationic analogues such as [(dipp)Ag(PCy3)][PF6]₂ and [(dipp)Cu(Ph3P)][PF6]₂.[30]

Encouraged by the successful chloride substitution and carbene transfer from (WCA-NHC)Li-toluene (1-toluene) onto [(Ph3P)MCl] (M = Ag, Cu), the preparation of phosphate-free WCA-NHC silver(II) and copper(I) complexes was attempted.

Hence, the reaction of 1-toluene with silver(I) trifluoromethane-sulfonate (AgOTf) afforded the toluene solvate [(WCA-NHC)Ag(toluene)] (5a) in 82% yield as a white crystalline solid after stirring for 10 min, filtration through Celite® and recrystallization from toluene/dichloromethane solution (Scheme 2). Longer reaction times produced significantly lower yields, which could tentatively be ascribed to ligand exchange and formation of ionic dicarbene-silver complexes as side products.[27] The corresponding copper complex 5b could be isolated from the reaction of 1-toluene with CuCl in toluene solution and was
isolated as a colorless crystalline solid in 91% yield after stirring for 16 h, filtration through Celite®, and recrystallization from toluene/diethyl ether solution. Gratifyingly, the Chem. Eur. J. drawn at 50 % probability level. All hydrogen atoms are omitted for clarity.  

Figure 5. Molecular structure of 5a with thermal displacement parameters drawn at 50% probability level. All hydrogen atoms are omitted for clarity. Pertinent structural data are assembled in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] of compounds 2–7.

| Complex | M−C1 | M−X | C1−M−X |
|---------|------|-----|-------|
| 2 (M = Ag, X = Cl) | 2.141(3) | 2.151(3) | 178.08(10) |
| 3 (M = Cu, X = Cl) | 1.877(3) | 2.133(6) | 175.59(9) |
| 4a (M = Ag, X = P) | 2.085(2) | 2.343(6) | 166.81(6) |
| 4b (M = Cu, X = P) | 1.9063(12) | 2.1926(4) | 166.23(4) |
| 5a (M = Ag, X = Cl) | 2.0839(14) | 2.3362(17) | 164.94(7) |
| 5b (M = Cu, X = Cl) | 1.9016(17) | 2.2013(19) | 163.53(8) |
| 6a (M = Ag, X = Cl) | 2.0907(14) | 2.5527(4) | 147.85(4) |
| 6b (M = Cu, X = Cl) | 1.898(3) | 2.6727(4) | 131.98(4) |
| 7 (M = Ag, X = I) | 2.139(5) | 2.8619(5) | 132.64(13) |

[a] Two independent molecules in the asymmetric unit.

atoms in a η1-fashion with Ag1–C46/C47 = 2.3382(17)/2.4056(17) Å and Cu1–C46/C47 = 2.2013(19)/2.1220(19) Å. This interaction is best classified as charge-transfer bonding, with η1-coordination typically observed for η-complexes of the late transition metals.32 Such interactions have been observed only for a small number of cationic silver(II) and copper(II) NHC complexes, which requires the presence of weakly coordinating counterions. Accordingly, the complex [[(TrAg)η1-C5H4F]2SbF6] was isolated from a fluorobenzene solution of [[TrAg(OTf)] in the presence of Na[BF4] (Tr = 1,3,5-tris(triﬂuoromethyl)-imidazol-2-ylidene, Ar′ = 3,5-bis(triﬂuoromethyl)phenyl). With silver-carbon distances of 2.115(3), 2.381(4) and 2.435(4) Å, this complex exhibits similar, but slightly longer Ag–C bond lengths compared to 5a.32 Likewise, the copper(II) complexes [[Dipp Cu(arene)]2[SbF6] (arene = η1-benzene, η1-C6Me6, η1-toluene, η2-m-xylene) were isolated by reaction of [[DippCuBr] with AgSbF6 in CH2Cl2/arene solution and feature η2- or η1-coordination modes in the solid state.32 Similar metal-arene interactions were also observed for coinage metal complexes of N-heterocyclic silenyl ligands.31

Originally, we envisaged that the silver(II) and copper(I) toluene complexes 5 might be ideally suited for WCA-NHC transfer to transition metals, with the ultimate goal to prepare ruthenium(II) WCA-NHC complexes for application in olein metathesis. Such systems could serve as anionic analogues of recently developed and commercialized cationic ruthenium olein metathesis catalysts bearing ammonium tags.31i It was found, however, that these complexes resisted the elimination of silver(I) and copper(I) halides, presumably because of their exceptionally strong metal-carbene bonds. Accordingly, the reactions 5a and 5b with [[η5-p-cymene]RuCl2(PPh3)] in toluene solution afforded the heterobimetallic complexes 6 as orange-crystalline solids in 69% (6a) and 97% (6b) yield after filtration through Celite® and recrystallization from dichloromethane/n-hexane solutions (Scheme 2). The NMR spectra show the presence of both the (WCA-NHC)M (M = Ag, Cu) and the (η5-p-cymene)Ru units, with the carbene carbon atoms giving rise to a doublet of doublets at 185.0 ppm with 1JAg,C = 275/317 Hz and to a singlet at 180.9 ppm in the 13C NMR spectra of 6a and 6b, respectively.

The heterometallic nature of the complexes 6 was confirmed by X-ray diffraction analysis; 6a crystallized as the solvate 6a·CH3Cl in the monoclinic space group P21/c, whereas 6b·CH3Cl crystallized in the orthorhombic space group Pbcn. The molecular structures are presented in Figure 6 (6a) and Figure S5 (6b, see the Supporting Information). The silver and copper atoms have strongly distorted trigonal-planar coordination spheres and are built into four-membered M(μ-Cl)2Ru rings (M = Ag, Cu), which are folded along the Cl−Cl diagonal with dihedral angles between the MCl2 and RuCl2 planes of 35.19(2)° (6a) and 35.99(5)° (6b). The WCA-NHC ligands adopt vertical orientations with respect to the MCl2 plane with the B(CF3)2 and p-cymene units facing in opposite directions. The metal-carbene bond lengths of 2.0970(14) Å (Ag1−C1) and 1.898(3) Å (Cu1−C1) are almost identical to those of the corresponding complexes 4 and 5 (Table 1). The Ag1–Ru1 and Cu1–Ru1 distances are 3.5995(2) Å (6a) and 3.3938(6) Å (6b), ruling out...
any significant metal-metal bonding as for instance found in cyclopentadienyl (Cp) ruthenium complexes of the type [II(dpp) MRuCp(CO)] (M = Ag, Ag–Ru = 2.607 Å; M = Cu, Cu–Ru = 2.439). It should be noted that examples of a controlled construction of halide-bridged heterobimetallic ruthenium-silver and ruthenium-copper complexes are rare, and we are only aware of cyclopentadiene-ruthenium dicarbonyl complexes containing bridging [II(dpp)MC1] (M = Ag, Cu) units as the only other examples of NHC-supported heterobimetallic Ru/Ag and Ru/Cu systems.

The resistance of complexes 6 to form a WCA-NHC-ruthenium complexes by elimination of AgCl or CuCl prompted us to study the reaction of the silver complex 5 with the corresponding iodine complex [η5-p-cymene]RuI[(PPh3)2] in dichloromethane, since the formation and precipitation of AgI might favour the formation of a metal-carbene complex. Surprisingly, however, the heterobimetallic Ag/Ru complex 7 was isolated as a red crystalline solid in 87 % yield after filtration through Celite® and recrystallization from CH2Cl2/n-hexane solution (Scheme 3). The presence of the (WCA-NHC)Ag moiety is evident from the 13C NMR signal at 182.8 ppm, which appears as the characteristic doublet of doublets with slightly smaller coupling constants of JAg,C = 254/290 Hz compared to the chlorido-bridged analogue 6a.

The molecular structure of 7 was determined by X-ray diffraction analysis, confirming the formation of a heterobimetallic Ag/Ru complex with bridging iodido ligands (Figure 7). In contrast to 6a, the four-membered Ag(μ-I)-Ru ring is close to planarity with a dihedral angle of 8.89(2)° between the Ag1 and Ru1 planes, which results in a significantly longer Ag1–Ru1 distance of 4.1057(5) Å. In contrast to 6a and 6b, the WCA-NHC ligand adopts a horizontal conformation and is almost perfectly aligned with the Ag1 plane. However, the NMR spectra indicate fast rotation of the WCA-NHC ligand in solution on the NMR timescale, in agreement with time-averaged C2-symmetry. It should be noted that, to the best of our knowledge, no other crystal structure of an iodido-bridged Ag/Ru complex has been reported to date.

Figure 6. Molecular structure of 6a with thermal displacement parameters drawn at 50% probability level. All hydrogen atoms and a disordered CH3Cl molecule are omitted for clarity. Two PPh3 phenyl rings are disordered over two positions, and only one orientation is shown. Selected bond lengths [Å] and angles [°] in 6a: Ru1–Cl1 2.4135(4)/2.4147(9), Ru1–Cl2 2.4156(3)/2.4088(9), Ru1–P1 2.3897(4)/2.3624(9), Cl1–M1–Cl2 78.629(12)/84.27(3), Cl1–Ru1–Cl2 86.129(13)/83.14(3), M1–C1–Ru1 93.461(13)/93.03(3), M1–Cl2–Ru1 89.901(12)/87.40(3). Other pertinent structural data are assembled in Table 1.

Figure 7. Molecular structure of 7 with thermal displacement parameters drawn at 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–Cl1 2.7263(4), Ru1–Cl2 2.7236(4), Ru1–P1 2.3677(12)/11, Ag1–Cl1 82.429(12), Ag1–Ru1–Cl2 86.986(12), Ag1–Cl1–Ru1 94.532(13), Ag1–Cl2–Ru1 95.299(13); Other pertinent structural data are assembled in Table 1.

Conclusion

With the synthesis and characterization of the complexes [(WCA-NHC)M(η5-toluene)] (5, M = Ag, Cu), we have again successfully exploited this class of anionic N-heterocyclic carbenes with a weakly coordinating borate moiety (WCA-NHC) for the generation of neutral analogues of otherwise cationic transition metal complexes for applications in nonpolar solvents. Accordingly, the high solubility of the complexes 5 in toluene and other aromatic hydrocarbons provides easy access to these and potentially numerous other silver(I) and copper(I) π-arene complexes. Attempts to use the complexes 5 as WCA-NHC transfer reagents were unsuccessful in the case of ruthenium(II); however, the observed transfer of the intact (WCA-NHC)M units enabled the isolation of the chlorido- and iodido-bridged heterobimetallic Ag/Ru and Cu/Ru complexes 6 and 7. While the latter complexes and related systems could find application in cooperative heterobimetallic catalysis, in
view of the enormous importance of (NHC)Ag and (NHC)Cu in catalysis,[20] it appears particularly promising to further exploit the potential of the complexes 5 to serve as homogeneous catalysts, especially in nonpolar solvents.

Experimental Section

All operations are performed in a glove box under a dry argon atmosphere (MBraun 2008) or on a vacuum line using Schlenk techniques. All solvents were distilled from Na/benzophenone or CaH2 degassed prior to use and stored over molecular sieves (4 Å). [(WCA-I-Dipp)Li(toluene)] and [Iq-p-cymene]RuCl3(PPh3) were prepared according to literature procedures. Full details of all analytical methods and experimental procedures can be found in the Supporting Information.

3.69–3.54 (m, 12 H, THF), 2.85 (sept, 3JN,N = 6.68 Hz, 4 H, CH(CH3)3), 1.78–1.70 (m, 12 H, THF), 0.72 (d, 3JH,H = 6.82 Hz, 12 H, CH3-CH). 1H NMR (160 MHz, THF-d8): δ [ppm] = –15.23 (s). 14C14H14(N) NMR (125 MHz, THF-d8): δ [ppm] = 183.9 (2 x d, 3JH,H = 224 Hz, 195 Hz, NCN), 150.5 (m, ar-CF3-C) 148.6 (m, 2 x CH2-CH), 146.9 (s, 4 x O-Dipp), 146.4 (s, 4 x O-Dipp), 140.0 (m, ar-CF3-C), 138.5 (s, 2 x Dipp), 138.1 (m, ar-CF3-C), 136.9 (s, 2 x Dipp), 127.2 (s, 2 x CH2-CH), 130.0 (s, 2 x O-Dipp), 124.6 (s, 4 x Dipp), 124.0 (s, 4 x Dipp), 68.0 (s, CH2-TiF), 28.4 (s, 4 x CH2(CH3)), 28.0 (s, 4 x CH2(CH3)), 27.8 (s, 4 x CH2(CH3)), 26.1 (s, CH2-TiF), 24.9 (s, 4 x CH2(CH3)), 23.3 (s, 4 x CH2(CH3)), 21.8 (s, 4 x CH2(CH3)). 13F13H NMR (376 MHz, THF-d8): δ [ppm] = –129.5 (br s, 6 F, o-PPh2), –163.8 (s, J = 20.3 Hz, 3 F, p-F). –168.2 (t, J = 18.7 Hz, 6 F, m-F).

[(WCA-I-Dipp)Li(toluene)] (1): A Schlenk flask is charged with [(WCA-I-Dipp)Li(toluene)] (1, 150 mg, 0.15 mmol, 1.0 equiv.) and AgCl2 (15.0 mg, 0.15 mmol, 1.0 equiv.) in THF (1 mL). The solution is stirred under vacuum for 2 h and then filtered through a layer of Celite®. The solvent is removed under high vacuum and the crude solid recrystallized from DCM/n-hexane to obtain product 4b as colorless crystals (130.0 mg, 0.10 mmol, 69%). Elemental analysis (%) calc. for C18H18AgBF4P2N4: C 51.65, H 4.00, Cl 5.01, Br 15.58, Ag 20.33, Br 15.58 s, (2 x i-Dipp), 135.9 (m, ar-CF3-C), 135.8 (s, 2 x i-Dipp), 130.4 (br s, CH2-CB), 130.1 (s, 2 x p-Dipp), 128.6 (s, 2 x p-Dipp), 124.1 (s, 2 x m-Dipp), 21.8 (s, 4 x CH2-TiF), 15.2 (s, 500 MHz, THF-d8): δ [ppm] = 7.46 (m, 5 H, PPh2), 7.32 (m, 8 H, PPh2, p-Dipp), 7.16 (d, 3JH,H = 6.80 Hz, 2 H, m-Dipp), 6.87 (m, 1 H, THF), 1.16–1.02 (m, 18 H, CH2-CH). 13F13H NMR (125 MHz, THF-d8): δ [ppm] = 177.2 (s, J = 14.8 Hz, o-PPh2), 132.2 (s, p-PPh2), 131.2 (br s, CH2-CB), 130.5 (d, J = 42.4 Hz, i-PPh2), 130.0 (d, J = 10.6 Hz, m-PPh2), 129.1 (s, p-PPh2), 128.7 (s, 2 x p-Dipp), 124.5 (s, 2 x m-Dipp), 123.8 (s, 2 x m-Dipp), 28.8 (s, 2 x CH2(CH3)), 28.4 (s, 2 x CH2(CH3)), 28.3 (s, 2 x CH2(CH3)).

[(WCA-I-Dipp)Li(toluene)] (1): A Schlenk flask is charged with [(WCA-I-Dipp)Li(toluene)] (1, 150 mg, 0.15 mmol, 1.0 equiv.) and suspended in toluene (8 mL). Chloro(triphenylphosphine)silver(I) (61.0 mg, 0.15 mmol, 1.0 equiv.) is added and the suspension is stirred for 2 h and then filtered through a pad of Celite®. The solvent is removed under high vacuum, and the crude product recrystallized from DCM/n-hexane to obtain product 4a as colorless crystals (130.0 mg, 0.10 mmol, 69%). Elemental analysis (%) calc. for C18H18AgBF4P2N4: C 51.65, H 4.00, Cl 5.02, Br 15.58, Ag 20.33, Br 15.58 s, C,Ag 35.01, P 11.69, CB, 130.1 (s, 2 x i-Dipp), 135.9 (m, ar-CF3-C), 135.8 (s, 2 x i-Dipp), 130.4 (br s, CH2-CB), 130.1 (s, 2 x p-Dipp), 128.6 (s, 2 x p-Dipp), 124.1 (s, 2 x m-Dipp), 21.8 (s, 4 x CH2-TiF), 15.2 (s, 500 MHz, THF-d8): δ [ppm] = 7.74–7.43 (4 m, 4 H, PPh2), 7.41 (d, 3JH,H = 7.7 Hz, 1 H, p-Dipp) 7.35–7.27 (m, 6 H, PPh2, p-Dipp), 7.27 (d, 3JH,H = 7.8 Hz, 2 H, m-Dipp), 7.08 (d, 3JH,H = 7.8 Hz, 2 H, m-Dipp), 6.95–6.85 (m, 6 H, PPh2), 6.47 (br s, 1 H, 7.37 (s, 6 H, CH2-CH). 1H AgBF4(N2): (ppm) = –129.3 (br s, 6 F, o-PPh2), –162.8 (t, J = 20.4 Hz, 3 F, p-F), –167.5 (t, J = 18.5 Hz, 6 F, m-F). HRMS (ES−)/m/z calcd for [(WCA-I-Dipp)LiCu]2+: C44H38BagC14F6N6: 997.1638, found 997.1628.
suspended in toluene (5 mL). CuCl (24.0 mg, 0.24 mmol, 2.0 equiv.) is added and the suspension is stirred for 10 minutes and then filtered through a pad of Celite®.

Elemental analysis (% calc. for C_{32}H_{48}BIC_{6}F_{7}N_{2}P_{3}Ru(Ph)_{3}Cl): C 58.98, H 4.12, N 1.73; F 97.41, H 6.12, H, Cl, C_{6}Cl_{4})(21.0 mg, 0.037 mmol, 1.0 equiv.) is added and the mixture is stirred for 16 h and then filtered through a pad of Celite®.

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Dipp), 128.9 (d, 1J=10.2 Hz, 6×m-PPh2), 124.0 (s, 2×m-Dipp), 123.2 (s, 2×m-Dipp), 108.3 (s, C8=C8-Cymene), 97.5 (s, C8=C8-Cymene), 90.0 (d, 1J=4.8 Hz, 2×CH2=Cymene), 87.4 (d, 1J=5.2 Hz, 2×CH2=Cymene), 31.2 (s, CH2(CH2)=Cymene), 28.7 (s, 2×CH2(CH2)=Dipp), 28.3 (s, 2×CH2(CH2)=Dipp), 27.5 (s, 2×CH2(CH2)=Dipp), 25.2 (s, 2×CH2=Cymene), 24.3 (s, 2×CH2=Cymene), 22.4 (s, 2×CH2=Cymene), 22.3 (s, 2×CH2=Cymene), 18.3 (s, CH2=Cymene). 19F{1H} NMR (376 MHz, dichloromethane-d2): δ ppm = −129.4 (for 6 F, o-F), −162.9 (s, J = 20.4 Hz, 3 F, p-F), −167.5 (s, 6 F, m-F). 13C{1H} NMR (162 MHz, dichloromethane-d2): δ ppm = −249.4 (s, CH=CPh). PRu): 533.07389, found 533.07396. Full Paper

Conflict of Interest

The authors declare no conflict of interest.

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