Synthesis of bis(σ-aryl)dirhodium(III) caprolactamates by oxidative arylation with arylboronic acids†‡

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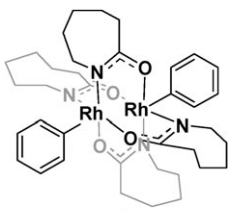
Recently discovered stable bis(σ-phenyl)dirhodium(III) caprolactamate and its substituted derivatives are conveniently prepared in high yields from dirhodium(II) caprolactamate and commercially available arylboronic acids in a copper-catalyzed process.

We recently reported the discovery of bis(phenyl)dirhodium(III) caprolactamate (**1**),[1] and characterized this novel dinuclear paddlewheel complex as the first unequivocal example of a dirhodium(III) compound. Extensive analyses established that **1** does not have a metal–metal bond. Although dimetal(III) compounds exist,[2] few have metal–carbon bonds with the most extensive listings being those of ruthenium[3] and osmium.[4] Diruthenium(III) organometallic structures have been constructed from 1-alkynes and stable diruthenium(III) compounds, and they have shown potential as molecular wires.[5] Arylrhodium(III) compounds are well known, but they are generally formed by transmetallation;[6] however, these same methods are not applicable to the formation of their paddlewheel dirhodium counterparts that include **1**.



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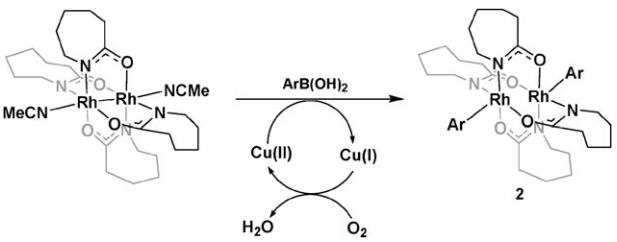
Bis(phenyl)dirhodium(III) caprolactamate (**1**) was prepared from either dirhodium(II) caprolactamate [$Rh_2(cap)_4$] or its oxidized dirhodium(II,III) analog with sodium tetraphenylborate using copper catalysis. Oxidative arylation does not occur in the absence of copper.[1] However, although sodium tetraphenylborate is commercially available, this compound and substituted tetraarylborates are difficult or impossible to prepare by known methods.[7] Consequently, we sought an alternative process for the synthesis of these compounds, and now report a convenient general methodology for the synthesis of bis(σ-aryl)dirhodium(III) caprolactamates in high yields.

With the wide availability and synthetic versatility of arylboronic acids,[8] we explored their possible utilization for the synthesis of bis(σ-aryl)dirhodium(III) caprolactamates (Scheme 1). When phenylboronic acid replaced sodium tetraphenylborate in the previously reported procedure [10 equiv. $PhB(OH)_2$, 15 mol% $(CuOTf)_2{\cdot}C_6H_6$, reaction in 4 : 1 CH_2Cl_2–MeOH], **1** was formed in modest yield (66%). Moderately strong bases aided complete product formation, and sodium methoxide was selected. Optimization of the reaction conditions showed that no reaction occurred in the absence of copper catalyst. The use of at least 5 equiv. of phenylboronic acid was required. When this reaction was performed at room temperature with the bis-acetonitrile complex of dirhodium(II) caprolactamate and 5.0 equiv. of phenylboronic acid in the presence of 15 mol% of [$(CuOTf)_2{\cdot}C_6H_6$] with 10 equiv. of sodium methoxide in 4 : 1 CH_2Cl_2–MeOH, **1** was isolated in 98% yield following a 12 h reaction time. A low yield of **1** (18%) was formed when phenylboronic acid 1,3-propylene glycol ester was used in place of phenylboronic acid, and there was no conversion to **1** with sodium phenyltrifluoroborate. Furthermore, only methanol promoted high product yields for **1**; a reaction performed with sodium methoxide in ethanol gave **1** in only 29% yield, and none of **1** was obtained from a reaction performed in 2-propanol.



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Scheme 1 Preparation of bis(σ-aryl)dirhodium(III) caprolactamates.

Representative arylboronic acids were surveyed to determine the generality of this procedure, and the results of this study are presented in Table 1. With the exception of the 4-dimethylaminophenyl-substituted product (**2g**), this methodology is tolerant of both electron-donating and electron-withdrawing substituents on the aromatic ring. Reaction times longer than 12 h showed no obvious advantage in product yield, but doubling the amount of arylboronic acid did provide modest increases in product yield in certain cases. However, arylboronic acids with *ortho* substituents (Me or MeO) did not undergo this reaction, nor did ferrocenylboronic acid and 2-furanylboronic acid.

Examination of the suitability of alternatives to the relatively expensive and air-sensitive $(CuOTf)_2{\cdot}C_6H_6$ was

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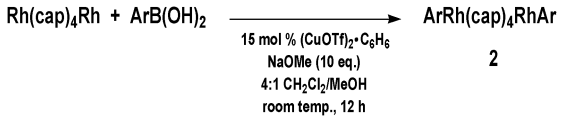
‡ Dedicated to Professor Andrew B. Holmes on the occasion of his 65th birthday.

Table 1 Copper(I) triflate catalyzed oxidative arylation of dirhodium(II) caprolactamate with arylboronic acids[a]



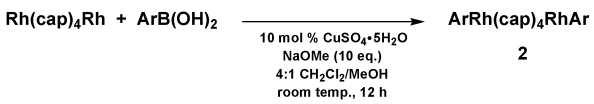
Compound	Ar =	equiv. $ArB(OH)_2$	**2**, yield %[b]
2a	3-$NO_2C_6H_4$	10	64
2b	3-$HCOC_6H_4$	10	54
2b	3-$HCOC_6H_4$	5	53
2d	4-$HCOC_6H_4$	10	99
2c	4-BrC_6H_4	5	91
2e	4-$MeOC_6H_4$	5	89[c]
2f	4-(BocNH)C_6H_4	10	71
2g	4-$Me_2NC_6H_4$	5	34
2h	3-Thiophenyl	5	72
2h	3-Thiophenyl	10	80[d]

[a] Reactions were performed at room temperature in 4 : 1 CH_2Cl_2–MeOH with 15 mol% $(CuOTf)_2{\cdot}C_6H_6$ and 10 equiv. NaOMe with a reaction time of 12 h. [b] Isolated yield after column chromatography on silica gel or crystallization from the reaction solution by trituration with methanol. [c] In a separate reaction under the same reaction conditions, the yield of **2e** was 87% after 24 h. [d] Reaction time was 24 h.

undertaken. Under the same conditions as reported in Table 1, but with only 10 mol% copper reagent, $Cu(OAc)_2{\cdot}H_2O$, $CuCl_2$, CuCl, CuBr and $CuSO_4{\cdot}5H_2O$ all gave the same yield of **1** (±2%) from the reaction between $PhB(OH)_2$ and $Rh_2(cap)_4$. Since these oxidations are catalytic only in the presence of molecular oxygen, the primary role of copper appears to be that of providing the Cu(II)/Cu(I) redox couple for the oxidation of Rh(II) to Rh(III).

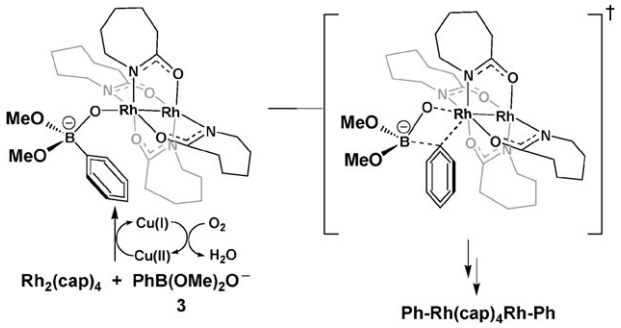
Based on the survey of copper catalysts suitable for oxidative arylation, copper(II) sulfate was selected as the most suitable. Results from the use of 10 mol% $CuSO_4{\cdot}5H_2O$ with $Rh_2(cap)_4$ and an array of representative boronic acids are described in Table 2. Even with the use of less copper (mol%) and reaction times of 12 h, product yields were consistently

Table 2 Copper(II) sulfate hydrate catalyzed oxidative arylation of dirhodium(II) caprolactamate with arylboronic acids[a]



Compound	Ar =	equiv. $ArB(OH)_2$	**2**, yield %[b]
2c	4-$HCOC_6H_4$	10	95
2i	4-$NO_2C_6H_4$	10	51
2j	4-$MeOOCC_6H_4$	10	97
2k	4-$F_3CC_6H_4$	10	96
2l	4-MeC_6H_4	5	92
2m	4-Ph-C_6H_4	5	93
2n	6-MeO-2-naphthyl	5	97

[a] Reactions were performed at room temperature in 4 : 1 CH_2Cl_2–MeOH with 10 mol% $CuSO_4{\cdot}5H_2O$ and 10 equiv. NaOMe with a reaction time of 12 h. [b] Isolated yield after column chromatography on silica gel.



Scheme 2 Phenyl transfer from boronate ester to rhodium.

greater than those when $(CuOTf)_2{\cdot}C_6H_6$ was employed. Arylboronic acids with both electron-donating and electron-withdrawing substituents were suitable substrates, but those with strong electron-withdrawing substituents like nitro in the *para* position led to a reduction in product yield. All of these compounds are air, water, and thermally stable.

Although mechanisms for aryl transfer involving π-complex formation between metals with an open coordination site and phenylboronates[9] or *via* boron metallocycles[10] are well known for rhodium(I) complexes, the evidence obtained from this study points to a scheme in which the aryl group is transferred from boron to rhodium through a boronate complex with the oxidized dirhodium(II,III) caprolactamate (Scheme 2). Solvolysis of the boronic acid is rapid[11] and expected to form **3** in equilibrium with other boronate species. The requirement of a species like **3** is consistent with the lack of reactions with phenylboronic acid ester or with sodium phenyltrifluoroborate. Furthermore, use of the dimethyl phenylboronic acid ester resulted in a 50% reduction in yield of **1**. Coordination of **3** with dirhodium caprolactamate and oxidation forms a rhodium(III) boronate complex that undergoes phenyl transfer from boron to give an intermediate monophenyl dirhodium complex that subsequently undergoes a second oxidative arylation reaction. The preference for methanol over other alcohol solvents suggests a significant steric effect for phenyl transfer.

The UV–visible spectra of these compounds exhibit a substituent-dependent absorption that is at or greater than 450 nm with electron-donating substituents and at or below 425 nm with electron-withdrawing substituents (Table 3). This spectral dependence suggests a distinct π-interaction through

Table 3 Spectral changes as a function of aryl substituent for representative bis(σ-aryl)dirhodium(III) caprolactamates[a]

Compound	Substituent	λ_{max} ($\varepsilon \times 10^{-3}$)[b]	^{13}C, δ (ppm)[c]
1	H	430 (4.5)	148.0 (d, 37.0 Hz)
2a	4-Me	440 (8.1)	142.8 (d, 37.0 Hz)
2m	4-Ph	440 (1.3)	146.6 (d, 37.0 Hz)
2c	4-HCO	422 (7.9)	161.5 (d, 37.0 Hz)
2j	4-MeOOC	425 (8.2)	157.6 (d, 37.0 Hz)
2k	4-CF_3	420 (4.2)	167.9 (d, 23.3 Hz)
2e	4-MeO	452 (6.2)	134.2 (d, 38.7 Hz)
2g	4-Me_2N	485 (3.0)	131.4 (d, 37.6 Hz)

[a] Spectral data for additional compounds can be found in Supplementary Information.† [b] λ_{max} in nm; ε in M^{-1} cm^{-1}. [c] Carbon bound to rhodium.

the phenyl ring onto the HOMO–LUMO of the bis(σ-aryl)-dirhodium(III) caprolactamates. Similarly, the ^{13}C chemical shift of the carbon directly attached to rhodium is also dependent on *para* substituents. With electron-withdrawing substitutions higher chemical shifts are observed; lower chemical shifts are found when *para* substituents are electron-donating. Except for that of **2k**, the J_{Rh-C} coupling constants from mononuclear phenylrhodium(III) are much lower than those reported here for bis(σ-aryl)dirhodium(III).[12]

In summary, a broad selection of bis(σ-aryl)dirhodium(III) caprolactamates is formed in high yield by copper(II) catalyzed reactions of arylboronic acids with dirhodium(II) caprolactamate, and their spectral properties suggest delocalization of aryl substituents to rhodium. The overall process is a net two one-electron transfers coupled with aryl transfer from arylboronic acid.

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Notes and references

1 J. M. Nichols, J. Wolf, P. Zavalij, B. Varughese and M. P. Doyle, *J. Am. Chem. Soc.*, 2007, **129**, 3504.
2 *Multiple Bonds Between Metal Atoms*, ed. F. A. Cotton, C. A. Murillo and R. A. Walton, Springer Science, New York, 3rd edn, 2005.
3 (*a*) S. K. Hurst and T. Ren, *J. Organomet. Chem.*, 2003, **670**, 188; (*b*) T. Ren, *Organometallics*, 2005, **24**, 4854.
4 T. Ren, in *Multiple Bonds Between Metal Atoms*, ed. F. A. Cotton, C. A. Murillo and R. A. Walton, Springer Science, New York, 3rd edn, 2005, ch. 10.
5 (*a*) J. L. Bear, B. Han and S. Huang, *J. Am. Chem. Soc.*, 1993, **115**, 1175; (*b*) G.-L. Xu, M. C. DeRosa, R. J. Crutchley and T. Ren, *J. Am. Chem. Soc.*, 2004, **126**, 3728; (*c*) Y. Shi, G. T. Yee, G. Wang and T. Ren, *J. Am. Chem. Soc.*, 2004, **126**, 10552; (*d*) J.-W. Ying, A. Cordova, T. Y. Ren, G.-L. Xu and T. Ren, *Chem.–Eur. J.*, 2007, **13**, 6874.
6 W. J. Hoogervorst, K. Goubitz, J. Fraanje, M. Lutz, A. L. Spek, J. M. Ernsting and C. J. Elsevier, *Organometallics*, 2004, **23**, 4550.
7 (*a*) N. A. Yakelis and R. G. Bergman, *Organometallics*, 2005, **24**, 3579; (*b*) V. Stavila, J. H. Thurston, D. Prieto-Centurión and K. H. Whitmire, *Organometallics*, 2007, **26**, 6864.
8 *Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine*, ed. D. G. Hall, Wiley-VCH, Weinheim, Germany, 2005.
9 (*a*) S. H. Strauss, *Chem. Rev.*, 1993, **93**, 927; (*b*) J. M. Forward, J. P. Fackler, Jr and R. J. Staples, *Organometallics*, 1995, **14**, 4194.
10 P. Zhao, C. D. Incarvito and J. F. Hartwig, *J. Am. Chem. Soc.*, 2007, **129**, 1876.
11 C. D. Roy and H. C. Brown, *J. Organomet. Chem.*, 2007, **692**, 784.
12 (*a*) H. Nishiyama, J. Ito, T. Shiomi, T. Hashimoto, T. Miyakawa and M. Kitase, *Pure Appl. Chem.*, 2008, **80**, 743; (*b*) Y. Motoyama, H. Narusawa and H. Nishiyama, *Chem. Commun.*, 1999, 131; (*c*) Y. Motoyama, M. Okano, H. Narusawa, N. Makihara, K. Aoki and H. Nishiyama, *Organometallics*, 2001, **20**, 1580.