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An Anionic Rhodium η^4-Quinonoid Complex as a Multifunctional Catalyst for the Arylation of Aldehydes with Arylboronic Acids

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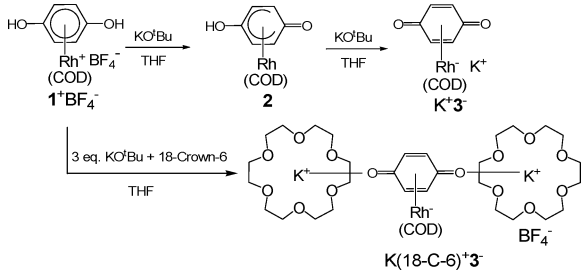
Complexes containing 1,4-hydroquinone (H_2Q) π-bonded to a transition metal are rather few in number but of substantial interest because of the importance of quinonoid molecules in mediating proton and electron transfer reactions.[1] Hydroquinone has been coordinated in an η^6-manner to the metal fragments $Cr(CO)_3$, $Mn(CO)_3^+$, and Cp^*M^{2+} (M = Rh, Ir).[2,3] The key chemical property displayed by these complexes is facile deprotonation of the −OH groups, which is accompanied by electron transfer to the metal and changes in the hapticity of the quinonoid ring.[3] This is illustrated in Scheme 1 for the new η^6-H_2Q complex $\mathbf{1}^+BF_4^-$, synthesized[4] in 74% isolated yield by the reaction of $[Rh(COD)Cl]_2$ with $AgBF_4$ and H_2Q. $\mathbf{1}^+BF_4^-$ cleanly undergoes deprotonation to afford stable neutral semiquinone (**2**) and anionic quinone ($\mathbf{3}^-$) complexes.

With a catalytically active metal, such as rhodium, it was thought that the ability to alter the charge on the metal by reversible deprotonation may constitute a simple way to tune catalytic activity. In addition, the anionic doubly deprotonated η^4-quinone complex $\mathbf{3}^-$ may be able to function as a ligand ("organometalloligand"),[5] thereby offering the possibility of bifunctional activation with appropriate substrates. Catalysts able to operate in a bifunctional manner are of considerable current interest.[6] Herein, it is demonstrated that the hydroquinone complex $\mathbf{1}^+BF_4^-$ is a convenient precursor to $M^+\mathbf{3}^-$, which serves as a catalyst for the coupling of arylboronic acids and benzaldehydes to produce diaryl alcohols (Scheme 2). It is shown that $M^+\mathbf{3}^-$ acts in a multifunctional manner by simultaneously activating both the boronic acid and the aldehyde, the former by coordination of a quinonoid oxygen in $\mathbf{3}^-$ to the boron and the latter through a Lewis acid interaction among the aldehyde, the counterion M^+, and a quinonoid oxygen.

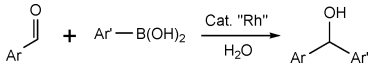
The X-ray structure of $[(H_2Q)Rh(COD)]BF_4 \cdot Et_2O$ established the anticipated η^6-bonding mode.[4] Deprotonation of $\mathbf{1}^+BF_4^-$ with KO^{t}Bu in THF occurred readily to afford the semiquinone (**2**) and the quinone ($K^+\mathbf{3}^-$) analogues (Scheme 1). X-ray quality crystals of $K^+\mathbf{3}^-$ could not be grown, but the butylammonium salt was readily obtained by metathesis and its X-ray structure determined as $Bu_4N^+[(1,4\text{-}Q)Rh(COD)]^- \cdot \mathbf{3}$ Bu_4NBF_4. The Rh−C bond lengths clearly indicated an η^4-bonding mode, with the quinone Rh−C distances being ca. 0.2 Å greater for the C(O) carbons in comparison to that of the other four quinone carbons.[4] Deprotonation of $\mathbf{1}^+BF_4^-$ with KO^{t}Bu in the presence of 18-crown-6 produced the salt $K(18\text{-}C\text{-}6)^+[(1,4\text{-}Q)Rh(COD)]^- \cdot K(18\text{-}C\text{-}6)BF_4$, in which each quinone oxygen is linked to a crown ether encapsulated potassium ion (Scheme 1).[7]

The cross-coupling of organoborates and organic electrophiles has become an important synthetic tool in organic chemistry.[8] While palladium is often used as the transition metal in the catalyst for this reaction, rhodium can also be effective. Especially noteworthy

Scheme 1. Deprotonation and Oxidation of Hydroquinone to Quinone with the π-Bonded Metal Fragment Acting as an Internal Electron Acceptor



Scheme 2. Catalytic Phenylation of Benzaldehydes



are the rhodium-catalyzed addition of arylboronic acids to aldehydes[9] and the 1,4-addition of arylboronic acids to enones.[10] The results obtained for arylboronic acid addition to benzaldehydes as catalyzed by rhodium quinone complexes are given in Table 1.

An inspection of the data in Table 1 shows some remarkable behavior. From entries 1−6, it is concluded that the cationic rhodium hydroquinone complex $\mathbf{1}^+BF_4^-$ has no catalytic activity, unless a base (KOH) is present. Addition of the neutral salt $K^+BF_4^-$ has no effect (entry 5). It is concluded that the base likely functions to deprotonate the −quinonoid −OH groups. In agreement with this, the anionic quinone complex $K^+\mathbf{3}^-$ was found to be a very effective catalyst, giving high yields at 75 °C or higher temperatures. Interestingly, the yield drops dramatically when a crown ether is added to the reaction mixture or when $K(18\text{-}C\text{-}6)^+\mathbf{3}^-$ is used as the catalyst in place of $K^+\mathbf{3}^-$ (entries 13 and 15). In a similar vein, the activity is reduced by the inclusion of $n\text{-}Bu_4N^+BF_4^-$ (entries 14 and 16). Likely related to this is the observation that $Li^+\mathbf{3}^-$ is a more effective catalyst than $K^+\mathbf{3}^-$, as indicated by entries 10 and 12 compared to 17 and 18. This behavior clearly signals heterobimetallic or dual function catalysis,[11,12] in which the alkali metal Li^+ or K^+ enhances the electrophilic activation of the aldehyde carbon by interacting with the carbonyl oxygen, thus facilitating aryl transfer from the rhodium catalyst, as depicted in **4**. This hypothesis is in accord with the reduced reactivity that is found when the alkali metal is chelated with a crown ether or is replaced with the much larger $n\text{-}Bu_4N^+$ ion.

Entries 7 and 30−33 show that electron-withdrawing para-substituents on the aryl group in $Ar'B(OH)_2$ hinder the reaction, as has been found with other catalyst systems.[9a] Table 1 also indicates that the catalytic conditions are tolerant of a wide range of aryl substituents in the aldehyde reactant (entries 8 and 24−29).

Suzuki−Miyaura-type coupling reactions involving boronic acids are usually facilitated by the presence of stoichiometric external

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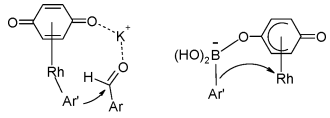
Table 1. Results of the Rhodium-Catalyzed Arylation of ArCHO with Ar′B(OH)$_2$ in Water Solvent[a]

entry	aldehyde	catalyst	additives (equiv)	*T* (°C)	time (h)	yield (%)[b]
1	C_6H_5CHO	$\mathbf{1}^+BF_4^-$	none	95	3	NR[c]
2[d]	C_6H_5CHO	$\mathbf{1}^+BF_4^-$	none	95	3	NR
3	C_6H_5CHO	$\mathbf{1}^+BF_4^-$	none	75	3	NR
4	C_6H_5CHO	$\mathbf{1}^+BF_4^-$	KOH (1.2)	75	3	97
5	C_6H_5CHO	$\mathbf{1}^+BF_4^-$	$K^+BF_4^-$ (1.2)	75	3	NR
6	C_6H_5CHO	$\mathbf{1}^+BF_4^-$	none	50	16	NR
7	C_6H_5CHO	$K^+\mathbf{3}^-$	none	95	3	96
8	C_6H_5CHO	$K^+\mathbf{3}^-$	none	75	3	93(90)
9	C_6H_5CHO	$K^+\mathbf{3}^-$	none	60	3	81
10	C_6H_5CHO	$K^+\mathbf{3}^-$	none	50	3	48
11	C_6H_5CHO	$K^+\mathbf{3}^-$	none	50	16	84
12	C_6H_5CHO	$K^+\mathbf{3}^-$	none	25	16	19
13	C_6H_5CHO	$K^+\mathbf{3}^-$	18-C-6 (0.075)	75	3	14
14	C_6H_5CHO	$K^+\mathbf{3}^-$	*n*-$Bu_4N^+BF_4^-$ (0.075)	75	3	24
15	C_6H_5CHO	K^+(18-C-6)$\mathbf{3}^-$	none	75	3	13
16	C_6H_5CHO	*n*-$Bu_4N^+\mathbf{3}^-$	none	75	3	2
17	C_6H_5CHO	$Li^+\mathbf{3}^-$	none	50	3	96(91)
18	C_6H_5CHO	$Li^+\mathbf{3}^-$	none	25	16	40
19	C_6H_5CHO	$[Rh(COD)Cl]_2$	none	75	3	NR
20	C_6H_5CHO	$[Rh(COD)]^+BF_4^-$	none	75	3	NR
21	C_6H_5CHO	$[Rh(COD)_2]^+BF_4^-$	KOH (0.025)	75	3	1
22	C_6H_5CHO	$[Rh(COD)_2]^+BF_4^-$	KOH (1.2)	75	3	99
23	C_6H_5CHO	none	KOH (1.2)	75	3	NR
24	4-$MeOC_6H_4CHO$	$K^+\mathbf{3}^-$	none	75	3	81(78)
25	2,4,6-$Me_3C_6H_2CHO$	$K^+\mathbf{3}^-$	none	75	3	69(68)
26	4-MeC_6H_4CHO	$K^+\mathbf{3}^-$	none	75	3	99(97)
27	4-ClC_6H_4CHO	$K^+\mathbf{3}^-$	none	75	3	99(97)
28	4-PhC_6H_4CHO	$K^+\mathbf{3}^-$	none	75	3	98(93)
29	4-$O_2NC_6H_4CHO$	$K^+\mathbf{3}^-$	none	75	3	99(92)
30[e]	C_6H_5CHO	$K^+\mathbf{3}^-$	none	75	3	96(91)
31[f]	C_6H_5CHO	$K^+\mathbf{3}^-$	none	75	3	94(90)
32[g]	C_6H_5CHO	$K^+\mathbf{3}^-$	none	75	3	20
33[h]	C_6H_5CHO	$K^+\mathbf{3}^-$	none	75	3	2

[a] Conditions: 2 mL of water, 0.025 mmol of catalyst, 1.0 mmol of aldehyde substrate, 1.2 mmol of Ar′B(OH)$_2$ (Ar′ = C_6H_5 for entries 1−29). [b] Yield determined by NMR; isolated yields in parentheses. [c] No reaction. [d] Solvent was *p*-dioxane (2 mL). [e] Ar′ = 4-$MeOC_6H_4B(OH)_2$. [f] Ar′ = 4-$MeC_6H_4B(OH)_2$. [g] Ar′ = 4-$ClC_6H_4B(OH)_2$. [h] Ar′ = 4-$O_2NC_6H_4B(OH)_2$.

base (e.g., compare entries 20 and 22).[8−10] It has been debated whether the base serves to increase the rate of transmetalation from boron to the transition metal catalyst by binding to the former or by binding to the latter. Recent theoretical studies suggest that the hard base OH$^-$ functions by binding to the electrophilic boron, and that this increases the rate of subsequent transmetalation.[13] The data in Table 1 show that $K^+\mathbf{3}^-$ and $Li^+\mathbf{3}^-$ are effective catalysts without the necessity of adding an external base. From this, we conclude that the $\mathbf{3}^-$ complex itself functions as the base by binding to the boron via the quinonoid oxygens, possibly as depicted in **5**.[14] The ability of the quinone ring system to undergo facile hapticity changes ($\eta^4 \rightarrow \eta^5$, etc.) may play a role in the ability of $\mathbf{3}^-$ to function as an organometalloligand in this manner. We conclude that catalyst $\mathbf{3}^-$ is able to act in a bifunctional (and cooperative) manner as has recently been suggested for other types of catalytic reactions.[6] In the present case, the binding of $\mathbf{3}^-$ to the boronic acid assists the transmetalation step by decreasing the electrophilicity of the boron and by placing the transition metal in the vicinity of the transferring group (Ar′).[15]



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In conclusion, we have characterized a π-bonded rhodium quinonoid complex that functions as a good catalyst for the coupling of arylboronic acids and aldehydes. The catalysis is *heterobimetallic* in that both the transition metal and concomitant alkali metal counterion play an integral part in the reaction. In addition, the anionic quinonoid catalyst itself plays a *bifunctional* role by acting as a ligand to the boronic acid and as a Lewis acid receptor site for the aryl group in the requisite transmetalation.

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Supporting Information Available: Experimental details, characterization and crystallographic (CIF) data, which have also been deposited with the Cambridge Crystallographic Data Center as registry number CCDC 274874−274875. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) See Supporting Information for details.
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(14) ^{1}H NMR spectra of $PhB(OH)_2$ in D_2O with and without $K^+\mathbf{3}^-$ present indicate that an interaction occurs.
(15) It should be noted that some Rh-catalyzed Suzuki−Miyaura couplings with suitable phosphine ligands do not require stoichiometric external base.[9a,b]

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