ORGANOMETALLICS
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Controlling Secondary Alkyl Radicals: Ligand Effects in Chromium-Catalyzed C−P Bond Formation

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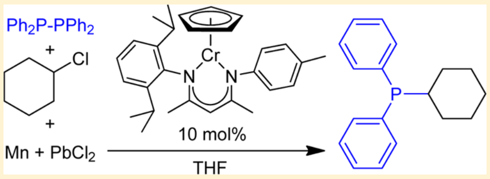
Supporting Information

ABSTRACT: Chromium cyclopentadienyl *β*-diketiminate catalysts have been used to form Ph_2PCy from Ph_2PY (Y = Cl, PPh_2, H) and CyX (X = Br, Cl) substrates. Manganese powder activated by PbX_2 or Me_3SiCl was used as the stoichiometric reductant. The Cr(III) cyclohexyl intermediate has been synthesized and structurally characterized. The observed variations in catalytic activity have been correlated with the previously observed reactivity differences imparted by modifying the N-aryl substituents on the *β*-diketiminate ancillary ligand.



First-row transition metals have found increasing use in the catalytic cross-coupling reactions of secondary alkyl halides.[1] For typical palladium catalysts, secondary R−X substrates are challenging due to slow rates of oxidative addition and competing *β*-elimination processes.[2] Many of the first-row metal-catalyzed cross-coupling reactions of secondary alkyl halides have been demonstrated to involve carbon-based radicals,[3] consistent with the long-known propensity of 3d organometallic species to engage in single-electron-transfer reactivity.[4] The introduction of reversible metal−alkyl bond homolysis provides exciting new options for catalysis, such as combining cross-coupling with radical intramolecular cyclization[5] and converting racemic secondary alkyl halide substrates to enantiomerically pure products.[2,6] Due to their ability to trap carbon-based radicals[7] and their stability with respect to *β*-H elimination,[8] it is often possible to isolate and characterize catalytically relevant first-row metal alkyl complexes despite their relatively weak M−R bonds.[9] This affords excellent opportunities to explore metal-mediated radical reactivity using well-defined complexes with readily modified ancillary ligands.[10]

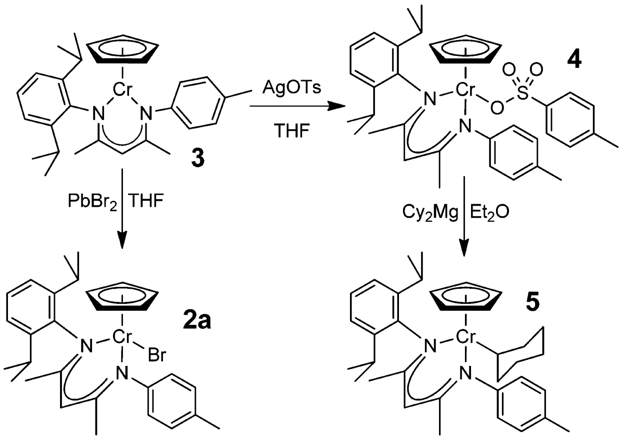
Transition-metal-catalyzed carbon−phosphorus bond-forming reactions have largely focused on $C(sp^2)$−P processes.[11] Recent work by the groups of Oshima and Studer has demonstrated the utility of radical C−P formation using tin and silyl reagents.[12,13] The titanium-mediated radical synthesis of Ph_2PCy from P_2Ph_4 and cyclohexyl bromide was recently developed by Cossairt and Cummins using stoichiometric $Ti[N(3,5\text{-}Me_2C_6H_3)tBu]_3$.[14] Although the three-coordinate Ti(III) reagent is a powerful single-electron reductant,[15] the Ti(IV) bromo product of halogen atom abstraction from CyBr is only slowly reduced back to the active Ti(III) species even using Na/Hg amalgam, effectively precluding a catalytic reaction.[14]

The ability of Cr(II) to trap carbon-based radicals is well-established[16] and forms the basis for several chromium-mediated reactions for organic synthesis.[17] Fürstner pioneered the use of manganese powder as a stoichiometric single-electron reductant for Cr(III) that is also compatible with organic halides.[18] We have recently been exploring the synthesis of well-defined paramagnetic $CpCr[(ArNCMe)_2CH](R)$ complexes,[19] the role of sterics in inducing Cr(III)−R homolysis, and their utility in controlling radical bond-forming reactions.[20] The Cr(III) $CpCr[(XylNCMe)_2CH](X)$ complexes (X = Br (**1a**), Cl (**1b**)) are effective catalysts for the radical cyclization of $C(sp^3)$−Br and $C(sp^3)$−Cl substrates.[21] To date, we have been unsuccessful in synthesizing secondary Cr(III) alkyls suitable for single-crystal X-ray diffraction with the symmetric xylyl-substituted ligand. The mixed N-aryl derivatives CpCr[DppNC(Me)CHC(Me)NTol](X) (X = Br (**2a**), Cl (**2b**)) are more suitable precursors for secondary alkyl complexes, due to the reduced steric demands of the *β*-diketiminate ligand.[22]

The desired Cr(III) complexes were prepared from the high-spin Cr(II) compound CpCr[DppNC(Me)CHC(Me)NTol] (**3**),[23] as shown in Scheme 1. The Cr(III) bromide **2a** was synthesized by single-electron oxidation of **3** with $PbBr_2$.[24] Oxidation of **3** with silver *p*-toluenesulfonate afforded the Cr(III) tosylate **4**, which was structurally characterized by X-ray diffraction.[25] As previously observed for the synthesis of related sterically demanding Cr(III) alkyl complexes,[19,20a] the most effective route to the Cr(III) cyclohexyl complex **5** utilized R_2Mg reagents with the Cr(III) tosylate precursor.[25] The X-ray crystal structure of **5** is shown in Figure 1. Although the Cr−C(cyclohexyl) bond length of 2.106(3) Å is longer than the $Cr−CH_3$ bond (2.01608(17) Å) of the corresponding Cr(III)

Received: August 31, 2012
Published: October 18, 2012

Scheme 1. Synthesis of CpCr[DppNC(Me)CHC(Me)Tol](X) Complexes (X = Br (2a), OTs (4), Cy (5))



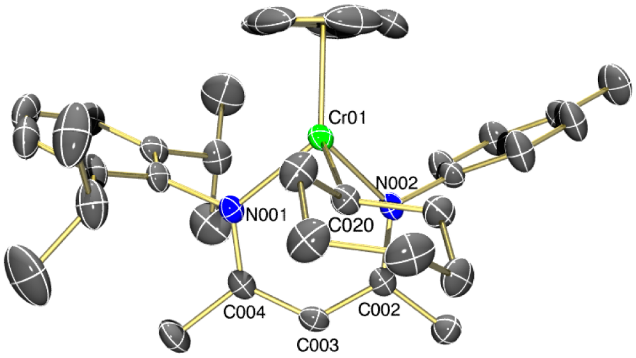
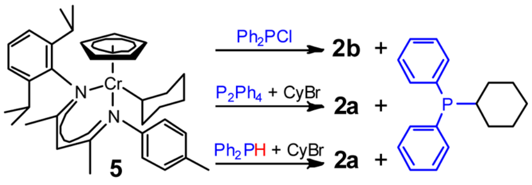


Figure 1. Molecular structure (50% thermal ellipsoids) of compound **5**. Hydrogen atoms have been removed for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Cr01−C020, 2.106(3); Cr01−N001, 2.057(2); Cr01−N002, 2.024(2); N001−Cr01−N002, 87.65(9); N001−Cr01−C020, 92.82(10); N002−Cr01−C020, 95.19(10).

Scheme 2. Stoichiometric Reactions of Cr(III) Cyclohexyl Complex 5 with Ph_2PY Reagents (Y = Cl, PPh_2, H)



Scheme 3

step 1 $\mathrm{[Cr]Cy \rightleftharpoons [Cr] + Cy^{\bullet}}$

step 2 $\mathrm{[Cr] + Ph_2PCl \longrightarrow [Cr]Cl + Ph_2P^{\bullet}}$

step 3 $\mathrm{Ph_2P^{\bullet} + Ph_2P^{\bullet} \longrightarrow P_2Ph_4}$

step 4 $\mathrm{P_2Ph_4 + Cy^{\bullet} \longrightarrow Ph_2PCy + Ph_2P^{\bullet}}$

step 5 $\mathrm{[Cr] + CyBr \longrightarrow [Cr]Br + Cy^{\bullet}}$

step 6 $\mathrm{Ph_2PH + Cy^{\bullet} \longrightarrow CyH + Ph_2P^{\bullet}}$

[Cr] = CpCr[ArNC(Me)CHC(Me)NAr′]

methyl complex,[23] it is in the range of 2.10−2.13 Å previously observed for primary alkyl ligands in $\mathrm{CpCr^{III}}$ complexes bearing symmetric 2,6-disubstituted *β*-diketiminate ligands.[19] The steric strain imposed by the secondary alkyl ligand in **5** is evident in the distortions of the N-aryl substituents away from the cyclohexyl group and the relatively long Cr−N(Dpp) and Cr−N(Tol) bonds of 2.057(2) and 2.024(2) Å, respectively. The UV−vis spectrum of **5** in hexanes displays the strong absorbance band at 553 nm characteristic of $\mathrm{CpCr[(ArNCMe)_2CH](R)}$ complexes.[19]

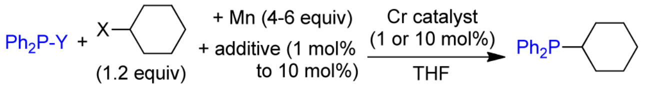
The reactivity of Cr(III) cyclohexyl **5** in stoichiometric reactions with Ph_2PY sources at room temperature in benzene was evaluated by ^{31}P NMR, with PPh_3 added as an internal standard (Scheme 2). Reaction of CpCr[DppNC(Me)CHC(Me)NTol](Cy) with Ph_2PCl resulted in the formation of Ph_2PCy in 94% yield (^{31}P NMR). Similarly, treatment of **5** with P_2Ph_4 and CyBr resulted in generation of Ph_2PCy in 96% yield (^{31}P NMR).[25] The corresponding reaction of **5** with CyBr and Ph_2PH resulted in a lower yield (30%) of Ph_2PCy. However, treatment of Ph_2PH with 2.2 equiv of CyBr and 2.7 equiv of the Cr(II) complex **3** produced 69% Ph_2PCy by ^{31}P NMR.[25]

Our working hypothesis for the reaction mechanism of these various $C(sp^3)$−P bond-forming processes is outlined in Scheme 3. In the absence of oxidants, small amounts of Cr(II) complex **3** can trap the radicals generated by the Cr−C bond homolysis of **5**, preventing the bimolecular reaction between two cyclohexyl radicals (step 1). However, Ph_2PCl reacts rapidly with **3** to form Cr(III) chloride **2b** and P_2Ph_4 (steps 2 and 3).[25] The consumption of the Cr(II) radical trap favors the production of cyclohexyl radicals, which then react with P_2Ph_4 (step 4).[12,13] Similarly, bromine atom abstraction from CyBr by Cr(II) generates Cr(III) bromide **2a** (step 5), also resulting in the rapid reaction of $Cy^{\bullet}$ with available P_2Ph_4 (step 4). The Cr(II) complex **3** does not react with P_2Ph_4, and attempts to prepare a Cr(III)−PPh_2 complex via salt metathesis reactions of $KPPh_2$ with **2a** or **4** were unsuccessful. The reaction of Cr(II) complex **3** with substoichiometric Ph_2PCl also produced only the Cr(III) chloride **2b**, P_2Ph_4, and unreacted **3**, indicating that if any Cr(III)−PPh_2 species is generated, it is unstable with respect to **3** and P_2Ph_4.

The key step in the overall reaction of **5** or **3** with CyBr and Ph_2PH is the rapid intermolecular hydrogen atom abstraction process shown in step 6,[26] which generates $Ph_2P^{\bullet}$ radical and cyclohexane. While the steps proposed in Scheme 3 remain speculative in the absence of mechanistic studies, the range of Ph_2PY substrates that can be employed to produce Ph_2PCy from Cr(III) cyclohexyl complex **5** attests to the flexibility of metal-mediated radical routes to $C(sp^3)$−P bond formation.

The stoichiometric reactions in Scheme 2 can be rendered catalytic by the use of $PbBr_2$-activated Mn powder[27] at ambient temperature and 1 mol % of the mixed N-aryl Cr(II) complex **3**, resulting in a 79% yield of Ph_2PCy from Ph_2PCl after 28 h (Table 1, entry 1). Comparable yields were obtained with catalyst **3** when the reaction was protected from ambient light[25] or when P_2Ph_4 and Ph_2PH were used as precursors (entries 2 and 3). In all cases, bipyridine was added at the completion of the reaction in order to displace Ph_2PCy from the paramagnetic $MnBr_2$ byproduct.[28−30] The catalytic activity of the symmetric $\mathrm{CpCr[(XylNCMe)_2CH]}$ Cr(II) complex **6** was assessed under the same reaction conditions. Although we have been unable to characterize the corresponding Cr(III) cyclohexyl complex by X-ray crystallography, due to its instability, the catalytic use of the bulkier 2,6-$Me_2C_6H_3$ disubstituted ligand led to an unexpected increase in the yields of Ph_2PCy from each phosphorus substrate (entries 4−6). A much lower yield of

Table 1. Chromium-Catalyzed Synthesis of Ph_2PCy^a



entry	Cr cat.[b]	CyX	Ph_2PY	additive[c]	yield,[d] %
1	**3**	CyBr	Ph_2PCl	$PbBr_2$	79
2	**3**	CyBr	P_2Ph_4	$PbBr_2$	70
3	**3**	CyBr[e]	Ph_2PH	$PbBr_2$	70
4	**6**	CyBr	Ph_2PCl	$PbBr_2$	92
5	**6**	CyBr	P_2Ph_4	$PbBr_2$	96
6	**6**	CyBr[e]	Ph_2PH	$PbBr_2$	83
7	**1a**	CyBr	Ph_2PCl	Me_3SiCl	82
8	**2a**	CyBr	Ph_2PCl	Me_3SiCl	76
9	**3**	CyCl	P_2Ph_4	$PbCl_2$	80
10	**6**	CyCl	P_2Ph_4	$PbCl_2$	29
11	**6**	CyCl	P_2Ph_4	$PbCl_2$	81

[a] The reaction temperature/time was 25 °C/28 h for entries 1−8, 55 °C/72 h for entries 9 and 10, and 55 °C/312 h for entry 11. [b] 1 mol % Cr catalyst was used for entries 1−8, and 10 mol % Cr catalyst was used for entries 9−11. [c] Catalytic PbX_2 (1−3 mol %) or Me_3SiCl (10 mol %) was added to activate Mn. [d] The yields were determined by ^{31}P NMR. [e] 2.4 equiv of CyBr was used with the Ph_2PH substrate.

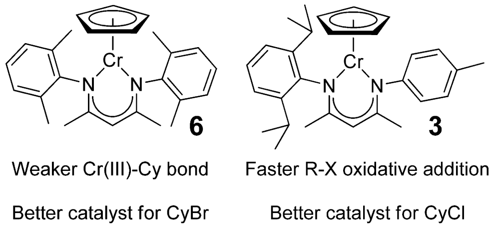
47% was obtained when 1 mol % Cp_2Cr was used as the catalyst, and no Ph_2PCy was observed by ^{31}P NMR when the reaction was conducted without chromium catalyst or when 10 mol % SmI_2 or $CrCl_3$ was used.[25] Interestingly, 32 mol % Ph_2PCy was obtained without Cr when 10 mol % of both NaCp and Li[DppNC(Me)CHC(Me)NTol] were added, suggesting that with the proper ancillary ligands a Mn-based catalyst may also be viable for this reaction.[25] Although related Ph_2PR complexes prepared by radical addition to P_2Ph_4 have been amenable to oxidation with H_2O_2 and purification by column chromatography,[13a] our initial attempts to isolate our product via this procedure were not successful.

While the Cr(II) complex **6** is highly air sensitive, it has been previously demonstrated that the Cr(III) μ-oxo oxidation product can be reduced back to the active Cr(II) form with Mn powder and substoichiometric Me_3SiCl.[31] As shown in entries 7 and 8, this strategy also allowed the air-stable Cr(III) bromide complexes **1a** and **2a** to be used as catalyst precursors in reactions that are set up in air and purged with N_2 prior to addition of the CyBr, Me_3SiCl, and Ph_2PCl.[25]

Less reactive secondary alkyl chlorides continue to pose a challenge as substrates for transition-metal-catalyzed reactions.[1,32] Although the reaction requires higher catalyst loading (10 mol % **3**), higher temperatures (55 °C), and longer reaction times (72 h), Ph_2PCy can be produced in 80% ^{31}P NMR yield from P_2Ph_4 and CyCl (entry 9). Interestingly, under these reaction conditions, the symmetric Cr(II) complex **6** gives only 29% yield along with 59% unreacted P_2Ph_4 after 3 days (entry 10), with 81% yield only being achieved after 13 days at 55 °C (entry 11).

As summarized in Chart 1, the observed variations in catalytic activity between **3** and **6** can be attributed to the reactivity differences imparted by modifying the β-diketiminate ligand. With the more reactive cyclohexyl bromide substrate, the higher yields obtained with catalyst **6** are presumably due to the weaker Cr−Cy bond in the more hindered Cr(III) secondary alkyl complex, favoring the formation of Ph_2PCy as shown in Scheme 3, step 4. However, as was previously observed in the catalytic radical cyclization of chloroacetals,[21] Cr(II) complex **6** only reluctantly reacts with unactivated $C(sp^3)$−Cl bonds. Due to its decreased steric requirements, **3** is much more reactive than **6** for the single-electron oxidative addition of alkyl halides.[22] This increased propensity for oxidative addition accounts for the relatively high activity of **3** with the more challenging cyclohexyl chloride substrate. The effect of altering the ancillary ligands on the catalytic reaction with other alkyl halide substrates is an intriguing subject for subsequent investigations.

Chart 1



In comparison to more traditional 4d metal catalysts, the use of earth-abundant first-row transition metals can provide not only a substantial decrease in catalyst cost but also complementary reactivity. In the case of secondary alkyl halide substrates,[3,33] this distinctive reactivity is often attributable to the generation of carbon-based radicals as an integral feature of the catalytic cycle. Despite its long history in organometallic chemistry,[4,7,8] metal-mediated radical reactivity is not central to the way organometallic chemists currently approach catalysis.[34] It is therefore encouraging that the study of well-defined organometallic complexes with readily modified ancillary ligands can be used to match catalyst and substrates in these reactions, as demonstrated in Chart 1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, tables, text, and figures giving crystallographic data for **4** and **5**, complete experimental details, and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canadian Foundation for Innovation, and the University of British Columbia for financial support. K.M.S. thanks Prof. Jason Masuda for helpful discussions.

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