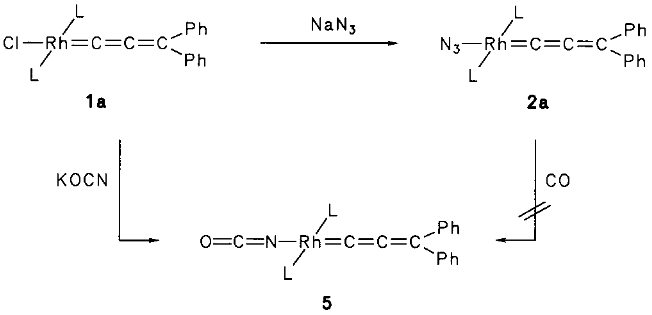
(=C=C=CRR′)(P*i*Pr$_3$)$_2$]. Therefore, one representative of this type of species was prepared by a different route (Scheme 2). Treatment of **1a** with excess KOCN in acetone/THF (1/1) at room temperature gives complex **5** as a red solid in 95% yield. Under the conditions used to form **3a**, **c** (in situ) and **3b**, **5** is completely inert toward CO. As far as N-bonded ligands are concerned, the reactivity of the Rh-bonded azido group in **2a–c** toward CO is unique. To the best of our knowledge, there is also no precedence for the type of C–N coupling which occurs during the conversion of **2a** and **2c** into **4a** and **4c**. With regard to the lability of the intermediate observed during the formation of **4a**, it is rather surprising that the related substituted alkynyl complex **3b** is completely inert and does not react either thermally or photochemically to afford *trans*-[Rh{C(CN)=C(Ph)*t*Bu}(CO)(P*i*Pr$_3$)$_2$]. Treatment of **4a** and **4c** with trifluoracetic acid results in cleavage of the Rh–C σ bond, leading to formation of the corresponding acrylonitrile derivatives R$_2$C=CHCN (R = Ph, An) in quantitative yields.



Scheme 2. L = P*i*Pr$_3$.

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Three-Component Coupling Reactions of Alkyl Iodides, 1,3-Dienes, and Carbonyl Compounds by Sequential Generation of Radical and Anionic Species with CrCl$_2$[**]

Kazuhiko Takai,* Naoto Matsukawa, Akira Takahashi, and Takafumi Fujii

Although conjugated dienes are good radical-trapping agents,[1] their use in organic synthesis is quite limited because further radical addition leading to polymerization occurs. Such radical chain reactions stem from the similar reactivity of the formed allylic radicals and the starting alkyl radicals. One way to prevent the undesirable side reactions is to reduce the allylic radicals to the corresponding anions (Scheme 1). However, a strong reductant such as samarium(II) readily reduces alkyl radicals, formed from alkyl halides, to furnish alkyl anions; the lifetime of the alkyl radicals is so short that intermolecular C–C bond formation cannot occur.[2, 3] We

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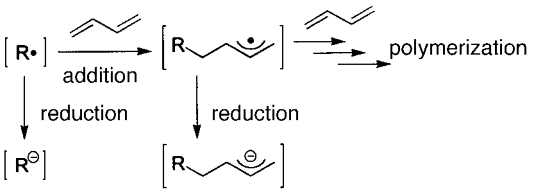
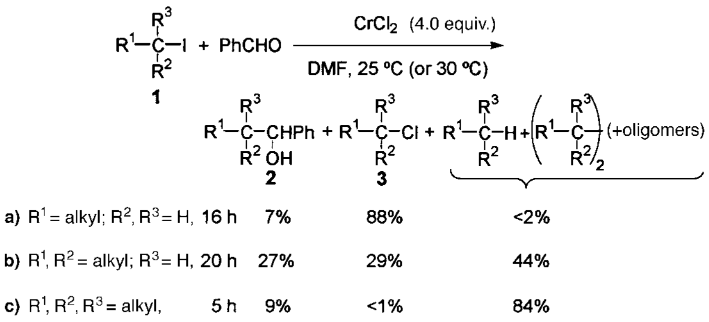


Scheme 1.



a) R^1 = alkyl; R^2, R^3 = H, 16 h 7% 88% <2%

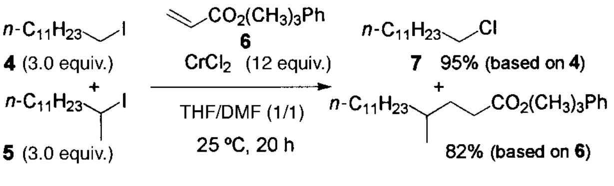
b) R^1, R^2 = alkyl; R^3 = H, 20 h 27% 29% 44%

c) R^1, R^2, R^3 = alkyl, 5 h 9% <1% 84%

report here that chromium(II) chloride, a mild reductant, can discriminate between alkyl iodides, alkyl radicals, and allylic radicals. As a result, 1) an alkyl radical has a sufficient lifetime to undergo intermolecular addition to a 1,3-diene, and 2) radical polymerization of the 1,3-diene can be suppressed by fast one-electron reduction of the allylic radicals. The sequential process of addition and reduction[4, 5] provides an allylic chromium species[6, 7] which adds to an aldehyde to afford a three-component coupling product.

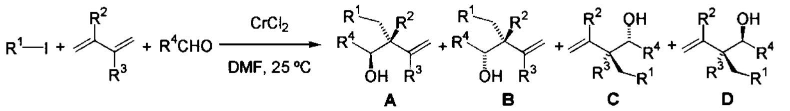
Chromium(II) salts are mild reducing agents, and reactive halides (such as allylic and benzylic halides) can be reduced to give the corresponding organochromium reagents.[8–10] However, it is more difficult to reduce simple alkyl halides in *aprotic* solvents. For example, treating a mixture of 1-iodododecane (**1a**, $R^1 = n\text{-}C_{11}H_{23}$, $R^2 = R^3 = H$) and benzaldehyde with $CrCl_2$ in DMF at 30 °C for 16 h afforded the Grignard adduct **2a** in only 7% yield, and most of the halide was recovered as 1-chlorododecane (**3a**).[4a] This result suggests that, in the case of primary alkyl iodides, the rate of substitution by the chloride ion is faster than that of one-electron reduction with a chromium(II) ion. In contrast, the reduction of secondary or tertiary alkyl iodides to form radical or anionic species proceeds smoothly under the same conditions.

Treating a mixture of the secondary alkyl iodide **1b** ($R^1 = n\text{-}C_{11}H_{23}$, R^2 = Me, R^3 = H) and benzaldehyde with $CrCl_2$ in DMF at 25 °C for 20 h gave the Grignard adduct **2b** and the alkyl chloride **3b** in 27 and 29% yield, respectively. Compounds derived from the alkyl radical (the dimer and the corresponding alkane) were also obtained in a combined yield of 44%. In the case of the tertiary alkyl iodide **1c** ($R^1 = n\text{-}C_{10}H_{21}$, $R^2 = R^3$ = Me), the Grignard adduct **2c** was produced in 9% yield, although most of the iodide was converted into the corresponding alkyl radicals. However, the formation of alkyl chloride **3c** was not observed. The intermediate alkyl radicals derived from the secondary iodide **5** could be trapped intermolecularly with the α,β-unsaturated ester **6** in 82% yield;[1,5,10b] the primary iodide **4** was recovered as the corresponding chloride **7** in 95% yield.



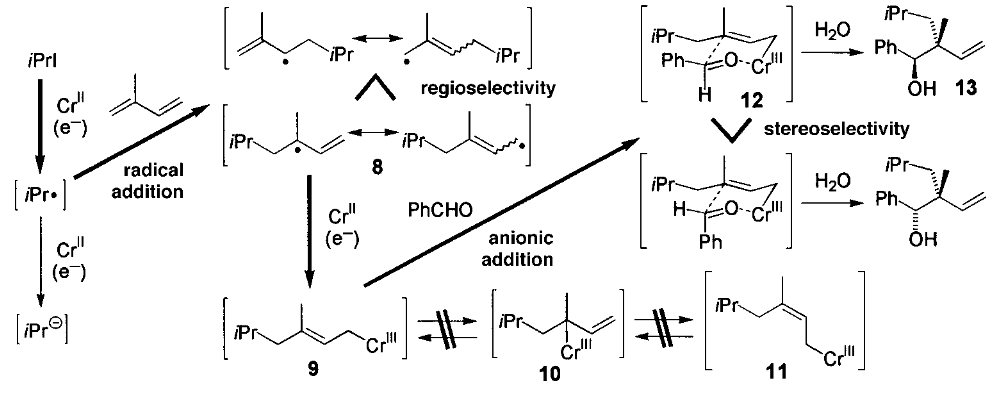
The secondary and tertiary alkyl radicals have a sufficient lifetime to undergo intermolecular addition to a 1,3-diene. Radical polymerization of the 1,3-diene did not occur, because fast one-electron reduction of the allylic radicals (leading to reactive allylic chromium species)[6, 7] took place smoothly. For example, treating a mixture of isopropyl iodide, isoprene, and benzaldehyde with $CrCl_2$ in DMF at 25 °C for 8 h produced two regioisomeric homoallylic alcohols in 53 and 13% yields, respectively (Table 1, entry 5). The major

Table 1. Three-component coupling of alkyl iodides, 1,3-dienes, and aldehydes.[a]



Entry	R^1	R^2	R^3	R^4	t [h]	Yield [%]	Regioselectivity	d.r.	
						A + **B** + **C** + **D**	(**A** + **B**):(**C** + **D**)	**A**:**B**	**C**:**D**
1	*t*Bu	Me	H	Ph	0.1	71	78:22	> 98:2	> 98:2
2	*t*Bu	Me	H	n-C_8H_{17}	0.1	96	78:22	> 98:2	96:4
3	*t*Bu	Me	Me	Ph	0.1	93	–	90:10	–
4	*t*Bu	Me	Me	n-C_8H_{17}	0.1	98	–	90:10	–
5	*i*Pr	Me	H	Ph	8	66	80:20	> 98:2	69:31
6	*i*Pr	Me	H	n-C_8H_{17}	8	91	77:23	> 98:2	67:33
7	*i*Pr	Me	H	n-C_8H_{17}	20	92[b]	68:32	79:21	68:32
8	*i*Pr	Me	H	c-C_6H_{11}	8	98	78:22	> 98:2	62:38
9	*i*Pr	Me	Me	Ph	8	71	–	81:19	–
10	*i*Pr	Me	Me	n-C_8H_{17}	8	88	–	80:20	–
11	*i*Pr	Me	Me	c-C_6H_{11}	8	91	–	82:18	–

[a] The reactions were conducted on a 1.0-mmol scale. The ratios of the isomers were determined by isolation, gas chromatography, and/or NMR spectroscopy. [b] The following amounts were used per mole of nonanal: chromium(II) chloride: 0.2 mol, manganese: 2.6 mol, Me_3SiCl: 3.7 mol. The reaction was conducted in DMF/THF (1/1).

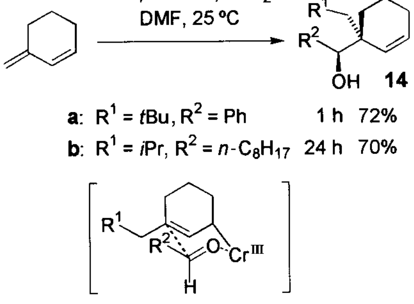


Scheme 2. Mechanism of the three-component coupling of alkyl iodides, 1,3-dienes, and aldehydes.

regioisomer contained one stereoisomer, which has isobutyl and hydroxyl groups in an *anti* geometry. The stereochemistry was determined by comparison with an authentic sample prepared by the Knochel procedure.[7] When *tert*-butyl iodide was used, the three-component addition proceeded within 10 min due to facile reduction of the iodide (entries 1–4). A catalytic system with chromium(II), manganese, and Me_3SiCl could also be employed for the three-component addition, although the regio- and stereoselectivities decreased slightly (entry 7).[11]

A mechanism which possibly explains the regio- and stereochemistry of the major isomer is shown in Scheme 2. An isopropyl radical preferentially adds to isoprene at the olefinic terminal on the side of the methyl group to form the most stable allylic radical **8**. Reduction of **8** produces the sterically favored extended allylic chromium reagent **9**. There is no fast equilibrium between the three allylic chromium compounds **9**, **10**, and **11** owing to the steric effect of γ,γ-disubstitution.[7] The chromium reagent **9** adds to benzaldehyde via the less sterically demanding six-membered transition state **12** to give homoallylic alcohol **13** selectively.[6, 7] This mechanism explains why diastereoselectivities for reactions with 2,3-dimethyl-1,3-butadiene (entries 3, 4, 9–11) are lower than for those with isoprene. Reduction of the steric difference by changing the β-substituent from H to Me decreases the selectivity of the extended allylic chromium reagents.

An example of the three-component addition to a cyclic compound is shown in Scheme 3. Because the stereochemistry of the allylic chromium reagent determines the configuration of an adduct with an aldehyde, fixation of a double bond by the cyclic system selectively produces only one of the stereoisomers **14**.



Scheme 3.

Experimental Section

Three-component coupling of isopropyl iodide, isoprene, and nonanal (Table 1, entry 6): To a mixture of $CrCl_2$ (0.74 g, 6.0 mmol)[12] in dry, oxygen-free DMF (12 mL) was added a solution of nonanal (0.14 g, 1.0 mmol), isoprene (0.20 g, 3.0 mmol), and isopropyl iodide (0.51 g, 3.0 mmol) in DMF (3 mL) at 25 °C. After the reaction mixture was stirred at 25 °C for 8 h it was poured into water (15 mL), and the mixture extracted with Et_2O (3 × 10 mL). The organic extracts were dried over anhydrous magnesium sulfate and concentrated. Purification by column chromatography on silica gel (hexane/Et_2O, 400/1) gave (3*R**,4*S**)-3-isobutyl-3-methyl-1-dodecen-4-ol in 70% yield (0.18 g) and 3-isobutyl-2-methyl-1-dodecen-4-ol in 21% yield (53 mg, *anti*:*syn* = 67:33).

14a: To a mixture of $CrCl_2$ (0.49 g, 4.0 mmol) in dry, oxygen-free DMF (7 mL) was added a solution of benzaldehyde (0.11 g, 1.0 mmol), 3-methylenecyclohexene (0.19 g, 2.0 mmol), and *tert*-butyl iodide (0.37 g, 2.0 mmol) in DMF (3 mL) at 25 °C. After the reaction mixture was stirred at 25 °C for 1 h it was poured into water (15 mL), and the mixture extracted with Et_2O (3 × 10 mL). The organic extracts were dried over anhydrous magnesium sulfate and concentrated. Purification by column chromatography on silica gel (hexane/Et_2O, 50/1) gave (1*R**,1′*R**)-(1-neopentyl-2-cyclohexenyl)(phenyl)methanol in 72% yield (0.19 g).

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First Isolation and Structural Characterization of Bis(Anthracene)Metal Complexes: $[Ti(\eta^6\text{-}C_{14}H_{10})(\eta^4\text{-}C_{14}H_{10})(\eta^2\text{-dmpe})]$ and $[Ti(\eta^4\text{-}C_{14}H_{10})(\eta^2\text{-}C_{14}H_{10})(\eta^5\text{-}C_5Me_5)]^-$**

John K. Seaburg, Paul J. Fischer, Victor G. Young, Jr., and John E. Ellis*

Dedicated to Professor Wolfgang Beck
on the occasion of his 65th birthday

Reagents that function as storable sources of "naked" metal atoms or highly unsaturated organometallic groups offer exciting new possibilities in chemical syntheses owing to their facile reactions with a variety of small molecules and their strongly reducing nature.[1] Of particular significance in this regard are fused-ring arenemetal(0) complexes, which are of substantial interest as possible precursors for the general exploration of zerovalent transition metal chemistry by virtue of the remarkable lability of these arene ligands.[2] Outstanding among these are bis(naphthalene)metal(0) species,[3] for which conventional syntheses were recently reported for the first time.[4] Basolo has presented evidence to suggest that bis(anthracene)metal(0) complexes may be even more labile than their naphthalene counterparts.[5] The only previously known complex of this type, bis(anthracene)chromium(0), was obtained as an inseparable mixture of complex and excess free anthracene by the cocondensation of chromium atoms and anthracene vapor in a metal atom reactor.[6] To our knowledge, no ligand exchange reactions of this compound have been reported to date. The dearth of information on potentially interesting bis(anthracene)metal complexes prompted an investigation of their possible conventional syntheses by the interaction of main group metal anthracenes with transition metal halides. Previously, this approach yielded only mono(anthracene)metal complexes.[7] We now report on the syntheses and molecular structures of the first well-characterized metal complexes containing two coordinated anthracene ligands: $[Ti(C_{14}H_{10})_2(dmpe)]$ (**1**, dmpe = 1,2-bis(dimethylphosphino)ethane) and $[Ti(C_{14}H_{10})_2(C_5Me_5)]^-$ (**2**, counterion $[K(18\text{-crown-}6)(thf)_2]^+$), THF = tetrahydrofuran). They are also of interest as the first structurally characterized Group 4 metal anthracene complexes.[8]

Reduction of $[TiCl_4(dmpe)]$ or $[TiCl_3(C_5Me_5)]$ by four equivalents of alkali metal anthracene (Na or K) in THF at −55 to −65°C gave deep red-brown or green-black solutions, from which **1** or $[K(18\text{-crown-}6)(thf)_2]$-**2** were isolated in 54% or 28% yield, respectively, as satisfactorily pure, diamagnetic and deep purple or black microcrystalline substances (see Experimental Section). Reactions of pure **1** (in the presence of an additional equivalent of dmpe) or **2** in THF at −55 to −65°C with normal pressures of carbon monoxide, under the same conditions described for the corresponding alkali metal naphthalene mediated carbonylations,[9,10] provided the known $[Ti(CO)_3(dmpe)_2]$ (**3**)[11] or $[Ti(CO)_4(C_5Me_5)]^-$(**4**)[12] in 57% or 62% yields, respectively, of product isolated as the $[K(18\text{-crown-}6)]^+$ salt. These syntheses, summarized in Equations 1 and 2, are very similar to previously reported

$$[TiCl_4(dmpe)] + 4\,NaC_{14}H_{10} \xrightarrow[-60\,^\circ C]{THF} \mathbf{1} \xrightarrow[\substack{dmpe\\ -55 \to 20\,^\circ C}]{THF,\ CO} \mathbf{3} \qquad (1)$$

$$[TiCl_3(C_5Me_5)] + 4\,KC_{14}H_{10} \xrightarrow[\substack{18\text{-}C\text{-}6\\ -60\,^\circ C}]{THF} \mathbf{2} \xrightarrow[-65 \to 20\,^\circ C]{THF,\ CO} \mathbf{4} \qquad (2)$$

naphthalene anion routes to these carbonyls and lend substantial credence to original suggestions that labile (naphthalene)metal complexes were involved in these and related carbonylation reactions.[13, 14] The anthracene complexes **1** and **2** appear to be substantially more stable in solution and the solid state than corresponding (naphthalene)titanium species, which could not be isolated as pure substances despite numerous attempts.[15] Nevertheless, at least in their reactions with carbon monoxide, **1** and **2** function as effective sources of

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