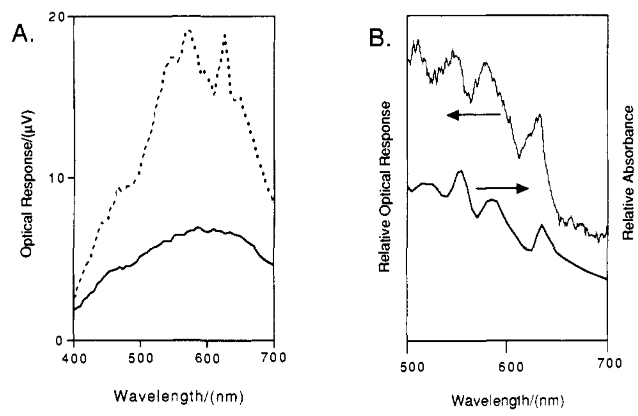

Figure 1. Optical response vs wavelength for a 3-mm-long × 50-μm-wide $YBa_2Cu_3O_{7-\delta}$ microbridge device operating at a temperature just below T_c(mid): (A) unprocessed signals for bare junction (lower curve) and junction coated with 3300 Å of octaethylporphyrin (upper curve); (B) comparison between the absorbance spectrum of an octaethylporphyrin film (1.1 μm thick) as measured by UV-visible spectrophotometry (lower curve) and the normalized optical signal of the dye–superconductor device with the uncoated junction response subtracted (upper curve).

In order to study the optical response of the device, the thin film assembly is mounted into an optical cryostat and one voltage and one current lead are attached to either side of the microbridge. After characterization by resistivity vs temperature, current–voltage experiments, and critical current measurements, the device is cooled down to just below the transition temperature of the superconductor film and a constant direct bias current is applied across the junction. The optical response of the dye–superconductor device is measured with a lock-in amplifier as a function of wavelength by monitoring the in-phase voltage which develops across the microbridge when chopped (20–25-Hz) monochromatic light is focused onto the junction area.

The unprocessed optical response at a $YBa_2Cu_3O_{7-\delta}$ microbridge with and without the octaethylporphyrin film is illustrated in Figure 1A.[7] In both cases, the largest response is recorded at around 600 nm, corresponding to the maximum throughput for the monochromator/quartz halogen light source combination. The bare junction exhibits a rather featureless response as has been described previously for similar systems.[4] The dye-coated superconductor structure, on the other hand, exhibits enhanced sensitivity as well as sharp features in the response curve that are absent for the bare junction. The frequencies at which enhanced responsivity occurs correspond to those wavelengths which are absorbed strongly by the dye film. Figure 1B provides a comparison between the absorption profile of the dye film and the response of the dye–superconductor microbridge. The latter has been normalized to the light intensity at a given wavelength, and the response of the uncoated junction has been subtracted. It is interesting to note that those wavelengths which are absorbed most strongly by the dye lead to the largest response for the hybrid dye–superconductor device. Thus, molecular dyes can be exploited to sensitize superconductor junctions to enhance both the responsivity[8] and the wavelength selectivity of the device. Moreover, since the normalized optical response of the composite device parallels the absorbance spectrum of the dye overlayer, the device can be exploited to measure the absorbance characteristics of a solid dye film.

To date we have prepared hybrid devices using dye films such as octaethylporphyrin (free base and copper), phthalocyanine, and rhodamine 6G. In all cases where degradation of the underlying superconductor was avoided, the molecular layer served to alter the response of the underlying superconductor structure in a reproducible fashion. Moreover, the magnitude of the response is greatest when the device is operated near T_c and no appreciable response is observed for $T > T_c$.[9]

With the discovery of the above-described hybrid dye–superconductor devices, new opportunities arise to study energy-transfer and electron-transfer phenomena which occur between molecules and superconductors. Work is now in progress to decipher the mode of operation of the hybrid devices and to expand upon the number and types of dyes that can be exploited to sensitize superconductor junctions.

Acknowledgment. This work was supported by the National Science Foundation (Presidential Young Investigator Program) as well as by the Electric Power Research Institute. We thank Professor Alex de Lozanne and his research group for technical assistance related to the deposition of superconductor thin films and Professors John White and Stephen Webber for use of a laser. We also gratefully acknowledge Matthew J. Holcomb for helpful discussion and Newport Corp. for a generous equipment donation.

Supplementary Material Available: Description of the procedure for fabricating composite dye–superconductor devices and plots of resistivity vs temperature, current vs voltage, dR/dT vs temperature, and optical response vs temperature for $YBa_2Cu_3O_{7-\delta}$ microbridge (7 pages). Ordering information is given on any current masthead page.

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[7] The optical response curves were recorded at a temperature of 48 K using a bias current of 5 mA. The transition-temperature midpoint for the device was 55 K.

[8] Since there was a small increase in the microbridge resistance following the dye deposition, some of the increase in signal for the dye-coated device may be attributed to this resistance increase.

[9] The temperature response of the hybrid device parallels dR/dT, which suggests that an indirect bolometric mechanism is operative for the system described herein (see ref 4).

New Triad Alkylation Reagent. Cross-Coupling of Indium Trialkyls with Alkenyl Halides

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Received September 17, 1991

Cross-coupling of metal alkyls with haloalkenes provides general and convenient method of preparing olefins. Among several organometallics already surveyed, organocopper reagents are the most powerful tool.[1] Additionally, Grignard or organozinc reagents with the assistance of transition metal catalysts have alternative values.[2] The scope of their power is somewhat limited to iodo- and bromoalkenes, and cross-coupling with chloroalkenes is seldom employed in practical synthetic applications. Further, the isomerization of carbanions is sometimes encountered in the cross-coupling of metal *sec*-alkyl derivatives.[2a] In order to get over such a limitation, aluminum alkyls and other group 13 organometallics must be applied further in the cross-coupling reactions, because they have greater tendency to form a Lewis complex with several chlorides in contrast to Grignard and organozinc reagents. Such complexation perhaps contributes to the activation of the chloride, promising a higher reactivity toward alkenyl chlorides without any isomerization through a dissociative cross-coupling manner.[4]

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[1] For reviews, see: (a) Posner, G. H. *Org. React.* (*N.Y.*) **1975**, *22*, 253. (b) Worm, A. T.; Brewstar, J. H. *J. Org. Chem.* **1970**, *35*, 1715.

[2] For reviews, see: (a) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669. (b) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340. (c) Negishi, E. *Organometallics in Organic Synthesis*; John Wiley & Sons: New York, 1980; Vol. 1, p 116. (d) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, p 713. (e) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, 1985.

[3] Mole, T.; Jeffrey, E. A. *Organoaluminum Compounds*; Elsevier: Amsterdam, 1972; p 111.

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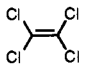
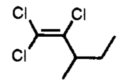
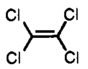
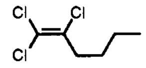
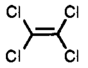
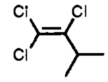
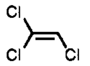
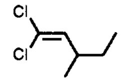
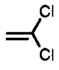
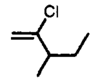
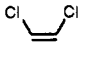
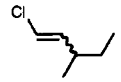
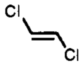
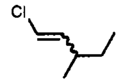
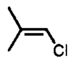
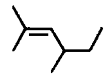
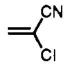
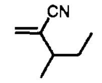
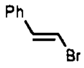
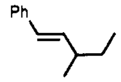
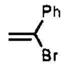
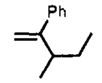
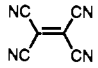
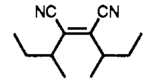
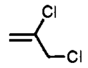
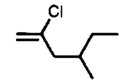
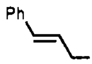
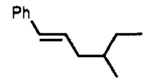
Table I. Cross-Coupling of Tri-*sec*-butylindium with Chloroalkenes[a]

InR_3	starting alkene	product	T/°C	t/h	% yield[b]
$InBu^s_3$			60	12	287
$AlBu^s_3$			60	12	40
Bu^sMgCl[c]			60	24	19
$InBu_3$			60	12	252
$InPr^i_3$			60	12	261
$InBu^s_3$			80	12	282
			0	12	210
			0	12	240[d]
			0	12	284[e]
			60	12	150[f]
			20	2	268
			30	12	206[f]
			0	3	(243)[g]
			60	12	112
			15	2	287
			−78	2	280

[a] Unless otherwise noted, 2 mmol of metal alkyl and 10 mmol of starting alkene were used, and the reactions were carried out without the use of any solvents under dry, deoxygenated N_2. [b] Isolated yields based on the amounts of metal alkyl employed. [c] Bu^sMgCl in THF (0.5 mol L^{-1} in THF) were used. [d] E/Z (61/39) mixture. [e] E/Z (67/33) mixture. [f] Partially polymerized during workup. [g] Isolated as poly(3-methyl-2-phenylpentene).

Previously, Negishi et al.[5] and Nozaki et al.[6] reported the stereospecific cross-coupling of aluminum alkyls with alkenyl halides and phosphates, etc. in the presence of transition metal catalysts. In the absence of catalysts, the cross-coupling of aluminum alkyls with chloroalkenes gave, however, unsuccessful results; for example, the reaction of tri-*sec*-butylaluminum with tetrachloroethylene gave 3-methyl-1,1,2-trichloropentene in only 40% yield as shown in Table I. In contrast, the reaction of tri-*sec*-butylindium (2.00 mmol) with tetrachloroethylene (10.0 mmol) at 60 °C for 12 h afforded 5.74 mmol of 3-methyl-1,1,2-trichloropentene and indium trichloride without the use of any catalysts and solvents.[7] Here we should point out that the percent yield based on the amount of indium trialkyl used reached 287%. This yield suggested that all three alkyl groups attached to a central In atom were effectively transferred to the product; in other words, indium trialkyls really acted as triad alkylating agents. All of the reactions of indium trialkyls with several chloroalkenes under similar conditions led to the selective formation of cross-coupled products in similar excellent yields as shown in Table I. Aluminum alkyls are generally known to offer only one-third of the alkyl groups originally attached.[9] Thus it should be emphasized again that all three alkyl moieties attached to In could be effectively consumed in these reactions. The difference is perhaps a result of the low bond strength of indium trialkyls and the large gap between ΔH_f° of MMe_3 and MCl_3; for example, $\bar{D}$(M–C) in $AlMe_3$ is reported as 283.3 kJ mol^{-1} while that in $InMe_3$ is 169.4 kJ mol^{-1},[10a] and $\Delta\Delta H_f^\circ$ for aluminum is −206 kJ mol^{-1} and for indium is −236 kJ mol^{-1}.[10b]

A stereospecific cross-coupling with (*E*)-*β*-bromostyrene proceeded to give (*E*)-*β*-*sec*-butylstyrene. In contrast, starting from both (*E*)- and (*Z*)-1,2-dichloroethylene, a mixture of (*E*)- and (*Z*)-1-chloro-3-methylpentene was obtained in a ratio of 6/4. This should suggest that the vinylic substitution proceeds via a multistep addition–elimination[11] type pathway. Cohen et al. reported that 1,2-dichloroethylene intrinsically shows a high π^*-LUMO level leading to a single-step substitution.[11b] The partial inversion may be rationalized by the following hypothesis: a Lewis complexation between indium trialkyl the dichloroethylene[3] enables free rotation of the C–C bond during the transition. Further, selective vicinal dialkylation occurred in the reaction of tetracyanoethylene, an alkene highly activated toward the substitution.[11]

On the other hand, indium trialkyls also displayed high reactivity toward allylic chlorides; e.g., 2,3-dichloropropene and cinnamyl chloride were effectively converted to 2-chloro-4-methyl-1-hexene and 4-methyl-1-phenyl-1-hexene, respectively. In these reactions no product via allylic rearrangement was detected. Benzyl chloride, however, would not give the cross-coupled product under similar conditions but a complex mixture of dibenzyl derivatives such as dibenzyl and butyl-substituted dibenzyls.[12,13]

Organoindium chemistry so far has not attracted much attention.[14] The results described in this article are the first ex-

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(4) Negishi, E. *Organometallics in Organic Synthesis*; John Wiley & Sons: New York, 1980; Vol. 1, p 351.

(5) Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729.

(6) Sato, M.; Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1609.

(7) The detailed reaction procedure is as follows: indium tri-*sec*-butyl (0.573 g, 2.00 mmol) was added dropwise to tetrachloroethylene (1.66 g, 10.0 mmol) with cooling by ice–water. The mixture was heated at 60 °C for 12 h with stirring. During the reaction, white precipitates gradually increased. Then the precipitates were filtered off, and the filtrate was fractionated by using Kugelrohr distillation under reduced pressure. Redistillation of the fraction (40–60 °C/15 Torr) gave the trichlorohexene (1.076 g, 5.74 mmol). The precipitates were revealed to be indium trichloride by a TG-DTA analysis. 3-Methyl-1,1,2-trichloro-1-pentene: colorless liquid, bp 75 °C/3.3 kPa; ^1H NMR ($CDCl_3$, 270 MHz) δ 3.05–3.16 (AM_2X_3 type m, 1 H, $J_{3,4}$ = 6.2 and $J_{3\text{-Me}}$ = 6.8 Hz, 3-H), 1.50 (quintet, 2 H, $J_{4,5}$ = 7.3 Hz, 4-H), 1.09 (d, 3-CH_3), 0.87 (t, 3 H, 5-H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 137.9 (s, 2-C), 116.3 (s, 1-C), 40.2 (d, 3-C), 27.7 (t, 4-C), 18.2 (q, 3-CH_3), 11.6 (q, 5-C); HRMS *m/z* 185.9785, calcd for $C_6H_9Cl_3$ 185.9770. Indium trichloride: very hygroscopic white powder, mp 586 °C (lit.[8] mp 586 °C).

(8) Ensslin, F.; Dreyer, H. *Z. Anorg. Allgem. Chem.* **1942**, *249*, 119.

(9) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, p 635.

(10) (a) Pilchner, G.; Skiner, H. A. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley: New York, 1982; p 69. (b) O'Neil, M. E.; Wade, K. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, p 8.

(11) (a) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (b) Cohen, D.; Bar, R.; Shaik, S. S. *J. Am. Chem. Soc.* **1986**, *108*, 231.

(12) The formation of the mixture of the dibenzyls was confirmed by GC–MS analysis.

(13) Recently we found that thermal decomposition of tri-*sec*-butylindium in methylarenes such as xylene and ethylbenzene proceeded through α-cleavage and that the corresponding dibenzyls were obtained via radical coupling; see: Nomura, R.; Miyazaki, S.-I.; Matsuda, H. *Organometallics* **1992**, *11*, 2.

amples that indicate that indium trialkyls can be employed in cross-coupling. Thus, we reveal the new organoindium characteristic of high alkylating power with triad efficiency, derived from a relatively strong Lewis acid nature and weak In–alkyl bond, which will be extensively available for organic synthesis in future.[15]

Supplementary Material Available: Spectral data of the cross-coupling products (2 pages). Ordering information is given on any current masthead page.

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(14) Most of the following articles reported the addition of organoindium compounds to unsaturated bonds: (a) Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1940**, *62*, 2353. (b) Clark, H. C.; Pickard, A. L. *J. Organomet. Chem.* **1967**, *8*, 427. (c) Tada, H.; Yasuda, K.; Okawara, R. *Inorg. Nucl. Chem. Lett.* **1971**, *28*, 21. (d) Maeda, T.; Tada, H.; Yasuda, K.; Okawara, R. *J. Organomet. Chem.* **1971**, *27*, 13. (e) Dolzine, T. W.; Oliver, J. P. *J. Organomet. Chem.* **1974**, *78*, 165. (f) Chao, L. C.; Riecke, R. D. *J. Org. Chem.* **1975**, *40*, 2253. (g) Araki, S.; Ito, H.; Katsumura, N.; Butsugan, Y. *J. Organomet. Chem.* **1989**, *369*, 291. (h) Nomura, R.; Fujii, S.; Matsuda, H. *Inorg. Chem.* **1990**, *29*, 4586. (i) Araki, S.; Shimizu, T.; Johar, P. S.; Jin, S.-T.; Butsugan, Y. *J. Org. Chem.* **1991**, *56*, 2538.

(15) One of the reviewers of this article has suggested the use of indium trialkyls in a one-pot procedure without the isolation of them. Our preliminary attempts indicated indium trialkyls generated in situ from indium trichloride and 1.5 equiv of Grignard reagents showed similar reactivities. We should state in addition that the indium trialkyls possess a stability almost equal to the corresponding aluminum alkyls.

One-Electron Oxidation of Cyclopentadienylchromium Carbonyl Hydrides: Thermodynamics of Oxidative Activation of Metal–Hydrogen Bonds toward Homolytic and Heterolytic Cleavage

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Received September 25, 1991

Organotransition-metal hydrides play a crucial role in important catalytic and stoichiometric processes.[1] The energetics of metal–hydrogen bond cleavage reactions have been extensively investigated,[2] often with great difficulty due to the lack of generally suitable methods. In organic chemistry, thermochemical cycles incorporating electrode potential data have gained widespread use for the extraction of otherwise inaccessible thermochemical data.[3,4] We have applied this methodology for the estimation of metal–hydrogen bond dissociation energies (BDEs)[5a,b] and metal hydride cation radical acidities[5c–e] in solution. A number of metal hydrides were activated toward deprotonation by 20 pK_a units or more as a result of a 1e oxidation.[5c,d] In this communication, we present the first estimates of M–H BDEs in metal hydride cation radicals and a comparison of the magnitudes of M–H activation toward homolytic and heterolytic cleavage resulting from 1e oxidation processes.

Table I. Metal Anion, Radical, and Hydride Oxidation Potentials[a]

metal center (M)	$E_{ox}(M^-)$[b]	$E_{ox}(M^\bullet)$[c]	$E_{ox}(M{-}H)$[c]
$CpCr(CO)_2(P(OMe)_3)$	−1.11	−0.21	+0.28
$CpCr(CO)_2(PPh_3)$	−1.29	−0.29	+0.12
$CpCr(CO)_2(PEt_3)$	−1.51	−0.37	+0.00
$Cp^*Cr(CO)_3$	−0.83	+0.19[d]	+0.55

[a] Volts vs Fc, determined by derivative cyclic voltammetry.[13] See Figure 1 caption for experimental conditions. [b] Reversible potentials, taken as the midpoints between anodic and cathodic waves. [c] Peak potentials for irreversible waves. [d] Somewhat broadened wave, perhaps reflecting a slow heterogeneous electron-transfer rate.

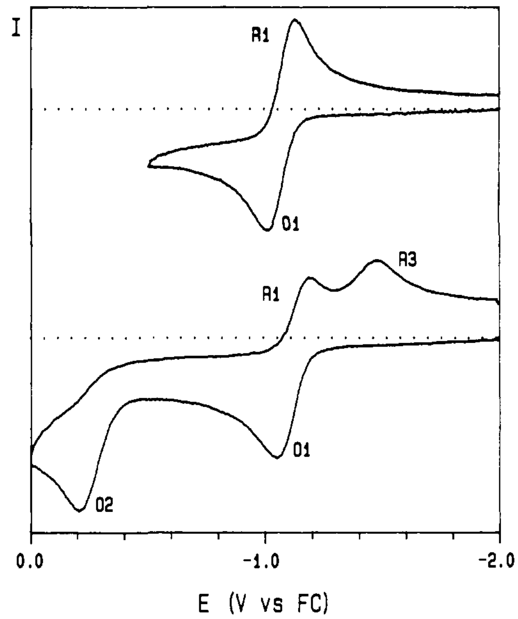

Figure 1. Cyclic voltammograms for the oxidation of $CpCr(CO)_2(P(OMe)_3)^-Et_4N^+$ (1.0 mM) in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ at a Pt disk electrode (d = 0.6 mm) at 25 °C and a voltage sweep rate ν = 1.0 V/s.

Scheme I

$$\begin{array}{lcll} & & & \Delta G^\circ \\ \hline M\text{-}H & \rightleftharpoons & M^\bullet + H^\bullet & BDE(M\text{-}H) \\ M^\bullet & \rightleftharpoons & M^+ + e^- & FE^\circ_{ox}(M^\bullet) \\ M\text{-}H^{\bullet+} + e^- & \rightleftharpoons & M\text{-}H & -FE^\circ_{ox}(M\text{-}H) \\ \hline M\text{-}H^{\bullet+} & \rightleftharpoons & M^+ + H^\bullet & BDE(M\text{-}H^{\bullet+}) \end{array}$$

$$BDE(M\text{-}H^{\bullet+}) = BDE(M\text{-}H) + F[E^\circ_{ox}(M^\bullet) - E^\circ_{ox}(M\text{-}H)] \quad (1)$$

The thermochemical cycle in Scheme I, analogous to one devised for the estimation of BDEs in organic cation radicals,[4c] may be used to determine M–H BDEs of metal hydride cation radicals. BDE(M–H) and BDE($M{-}H^{\bullet+}$) represent the BDEs of the neutral hydride and its cation radical, and E_{ox}(M–H) and $E_{ox}(M^\bullet)$ represent the oxidation potentials of the hydride and the corresponding 17e radical.[6a,7]

Rapid radical dimerizations[8] usually preclude the determination of $E_{ox}(M^\bullet)$. However, the hydrides $CpCr(CO)_2(PR_3)H$ (R = OMe, **1a**; Ph, **1b**; Et, **1c**) and $Cp^*Cr(CO)_3H$ (**1d**)[9] represent cases

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(6) (a) The resulting BDE(M–H) − BDE($M{-}H^{\bullet+}$) difference translates to enthalpy values since entropy changes may be safely assumed to cancel.[6b] (b) Kanabus-Kaminska, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311.

(7) This method may be used to estimate the magnitude of BDE(M–X) − BDE($M{-}X^{\bullet+}$) for any σ-bonded ligand X.

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