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Transition metal-organoindium chemistry. Reaction of trialkylindium compounds with (cyclopentadienyl)(tricarbonyl)metal radicals *

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Abstract

Photolysis of $[CpMo(CO)_3]_2$ with InR_3 (R = ethyl, t-butyl, neopentyl) or ZnR_2 (R = ethyl) efficiently forms $CpMo(CO)_3InR_2$ or $[CpMo(CO)_3]_2Zn$ as major products. The reaction is believed to proceed by bimolecular radical substitution and demonstrates substantial strength for the Mo-In bond. As a consequence of this bond strength, $[CpMo(CO)_3]_2$ reacts photochemically and reversibly with indium metal to form $[CpMo(CO)_3]_3In$.

Introduction

Modern semiconductor technology relies on volatile organoaluminum, -gallium, and -indium compounds as sources of these elements in the synthesis of III-V semiconductors [1]. Crucial to these processes are reactions that cleave metal-carbon bonds. A derivative topic that has been pursued in this laboratory is the use of transition metal compounds to provide new reaction patterns for cleaving main-group metal-carbon bonds. In earlier work we discussed indium- and zinc-carbon bond cleavage by oxidative addition reactions with several Ir, Rh, Pt compounds [2]. More recent investigations have concentrated on reactions of organoindium compounds with (tricarbonyl)(cyclopentadienyl)(molybdenum)- or (tungsten) compounds. With these transition metal compounds, radical or atom-transfer or electron-transfer reactions dominate over two-electron oxidative addition, and photochemically initiated radical substitution reactions are described in this article.

Results

Benzene solutions of $[CpM(CO)_3]_2$ (Cp = cyclopentadienyl; M = Mo, W) and trialkylindium compounds (alkyl = methyl, ethyl, t-butyl, neopentyl) are unreactive

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* Contribution No. 5116.

at mild temperatures (up to 35 °C) under an inert atmosphere in the dark. However, exposure to light causes a very rapid reaction between $[CpM(CO)_3]_2$ and triethyl-, tri-t-butyl-, or trineopentylindium. The photoreaction is reasonably straightforward if 577 nm light is used, and the bulk of the reaction proceeds according to Eq. 1a for $[CpMo(CO)_3]_2$ and excess $InEt_3$ in C_6D_6. The quantum yield for loss of $[CpMo(CO)_3]_2$ by Eq. 1a is quite high, 0.40 ± 0.07 at 577 nm in benzene. One complication is that a thermal equilibrium is established among $[CpMo(CO)_3]_x InEt_{3-x}$ species according to Eqs. 2, well known for alkylgallium and -thallium compounds [3–7] although only $[CpM(CO)_3]_3In$ (M = Mo, W) has been reported for In itself [8,9]. Thus while $CpMo(CO)_3InEt_2$ is presumably the major initial product of the photoreaction, the derivative compounds $[CpMo(CO)_3]_2InEt$ and $[CpMo(CO)_3]_3In$ form rapidly, in equilibrium amounts that involve the remaining triethylindium. A second complication is that the product distribution depends upon the amount of triethylindium present: The major molybdenum-containing product is $CpMo(CO)_3InEt_2$ when $InEt_3$ is present in excess, Eqn. 1a, but as the starting ratio of triethylindium to $[CpMo(CO)_3]_2$ becomes smaller, increasing amounts of $CpMo(CO)_3Et$ appear in the photoproducts along with $[CpMo(CO)_3]_xInEt_{3-x}$ ($x = 1$–3). In the extreme case of attempting exhaustive photochemical dealkylation in solution, where all the organoindium is to be converted to $[CpMo(CO)_3]_3In$, the stoichiometry approaches that of Eq. 1b.

$$[CpMo(CO)_3]_2 + \text{excess } InEt_3 \rightarrow 2\ CpMo(CO)_3InEt_2 + \{C_2H_4,\ C_2H_6,\ C_4H_{10}\} \tag{1a}$$

$$3\ [CpMo(CO)_3]_2 + InEt_3 \rightarrow 3\ CpMo(CO)_3Et + [CpMo(CO)_3]_3In \tag{1b}$$

$$2\ [CpMo(CO)_3]InEt_2 \rightleftharpoons InEt_3 + [CpMo(CO)_3]_2InEt \tag{2a}$$

$$2\ [CpMo(CO)_3]_2InEt \rightleftharpoons [CpMo(CO)_3]_3In + [CpMo(CO)_3]InEt_2 \tag{2b}$$

$$[CpMo(CO)_3]InEt_2 + [CpMo(CO)_3]_2InEt \rightleftharpoons InEt_3 + [CpMo(CO)_3]_3In \tag{2c}$$

With other organoindium compounds, different product distributions are obtained. $[CpMo(CO)_3]_2$ and excess $In(^tBu)_3$ react photochemically to form CH_2CMe_2, $HCMe_3$, and $CpMo(CO)_3In(^tBu)_2$. $[CpMo(CO)_3]_2$ and $In(CH_2CMe_3)_3$ slowly form $CpMo(CO)_3In(CH_2CMe_3)_2$ and a compound assigned as $CpMo(CO)_3CH_2CMe_3$, although this latter compound is unstable in solution and decomposes to unidentified products in 1–2 hours. Trimethylindium and $[CpMo(CO)_3]_2$ do not react photochemically. With organozinc compounds, comparable reactions are observed: Dimethylzinc and $[CpMo(CO)_3]_2$ do not react photochemically; diethylzinc and $[CpMo(CO)_3]_2$ photochemically form $[CpMo(CO)_3]_2Zn$ [10,11] and some $CpMo(CO)_3Et$, ethylene, ethane, butane, and small amounts of a species believed to be $CpMo(CO)_3ZnEt$. The tungsten dimer $[CpW(CO)_3]_2$ behaves analogously to the molybdenum dimer. All these reactions are quite clean; the indicated products account for > 95% of the materials present in solution. Owing to the equilibria of Eqs. 2 or their analogs, and the volatility of $InEt_3$ and $ZnEt_2$, only the fully metallated compounds $[CpMo(CO)_3]_3In$ and $[CpMo(CO)_3]_2Zn$ have been isolated [8–10]. The other compounds have been identified in solution by comparing ^1H NMR spectra with those of standard reaction mixtures (see Experimental Section).

Photochemical reactions are also observed between $[CpFe(CO)_2]_2$ and $InEt_3$ or $ZnEt_2$ except that these reactions are neither as rapid nor as clean as those of $[CpMo(CO)_3]_2$. The photoreaction between $[CpFe(CO)_2]_2$ and $InEt_3$ produces a mixture of several products that have not been identified, but the major product of the photoreaction with $ZnEt_2$ is $[CpFe(CO)_2]_2Zn$ [10].

The mechanism that appears most likely is summarized in Eqs. 3 for $[CpMo(CO)_3]_2$ and triethylindium. Photolysis of $[CpMo(CO)_3]_2$ produces $CpMo(CO)_3$ radicals which then attack $InEt_3$ in a bimolecular process [12] (Eq. 3a) with loss of ethyl radical. The ethyl radicals react either with themselves to form C_2H_4, C_2H_6, and C_4H_{10} (Eq. 3b) [13] or with $CpMo(CO)_3$ to form $CpMo(CO)_3Et$ (Eq. 3c). (A similar initial reaction is likely for $CpMo(CO)_3$ with other trialkylindium compounds, but the different organic radicals form different product compounds.) Actual rates of reactions 3 depend on several factors, including rate of generation of $CpMo(CO)_3$ radicals (a function of light intensity) and concentration of $InEt_3$, and a detailed kinetic analysis has not been attempted.

$$CpMo(CO)_3 + InEt_3 \rightarrow [CpMo(CO)_3]InEt_2 + Et \qquad (3a)$$

$$Et + Et \rightarrow C_2H_4, C_2H_6, C_4H_{10} \qquad (3b)$$

$$CpMo(CO)_3 + Et \rightarrow CpMo(CO)_3Et \qquad (3c)$$

Note that the indium–molybdenum bond is formed at the expense of an indium–carbon bond in Eq. 3a. The indium–molybdenum bond strength is evidently comparable to that of the indium–indium bonds of indium metal, as photolysis of a benzene solution of $[CpMo(CO)_3]_2$ in the presence of metallic indium (deposited by UV photolysis of $In(^tBu)_3$ [14]) dissolves the indium metal to form $[CpMo(CO)_3]_3In$. (Several hours of photolysis are required for a thin indium film to dissolve completely, while under comparable photolysis conditions the solution-phase reaction between $[CpMo(CO)_3]_2$ and $InEt_3$ is complete within minutes.) The photoreaction between $[CpMo(CO)_3]_2$ and metallic indium is partially reversible: Photolysis of $[CpMo(CO)_3]_3In$ at 435 nm restores some $[CpMo(CO)_3]_2$, identified by its visible absorption and by its ^1H NMR spectrum. Other C_5H_5-containing materials are also formed but have not been identified; in addition, a fine gray material is formed in suspension, which contains indium but which has not been fully characterized. In one experiment both processes were demonstrated: A benzene solution of $[CpMo(CO)_3]_3In$ was photolyzed (435 nm) until a considerable amount of $[CpMo(CO)_3]_2$ had been formed, presumably together with the corresponding quantity of elemental indium; subsequent photolysis (577 nm) decreased the amount of $[CpMo(CO)_3]_2$ and restored some $[CpMo(CO)_3]_3In$. Note that $[CpMo(CO)_3]_2$ by itself is photostable under these conditions.

Discussion

The reactions of $CpMo(CO)_3$ with trialkylindium compounds were examined for two reasons. First, after studying two-electron oxidative addition of trialkylindium compounds to low-valent iridium and platinum compounds, it was interesting to compare reactions of trialkylindium compounds with one-electron transition metal donors, and photogenerated $CpMo(CO)_3$ seemed a promising candidate. Second, we wondered how many In–C bonds could be cleaved using transition metal compounds, starting from InR_3. In our earlier study [2], iridium or platinum compounds removed only a single alkyl group from trialkylindium compounds, forming singly metallated $M–InR_2$ species. But $CpM(CO)_3$ compounds (in particular the hydrides, M = Mo, W) are known to cleave all three In–C bonds of trialkylindium compounds, forming alkane and triply metallated $In[CpM(CO)_3]_3$ [5–7].

Broad-band irradiation of solutions containing $[CpMo(CO)_3]_2$ and $InEt_3$ using the unfiltered beam from a 1000-watt Hg/Xe lamp produced a complicated mixture of products, but narrow-band irradiation at 577 nm (using an interference filter to isolate the Hg line) provided much simpler product mixtures (see Eqs. 1). Light of this wavelength was chosen because only $[CpMo(CO)_3]_2$ absorbs it, and trialkylindium compounds and the photoproducts do not: $[CpMo(CO)_3]_xInR_{3-x}$ compounds are colorless for $x = 0–2$, and yellow (transparent beyond 500 nm) for $x = 3$, and photostable at 577 nm in the absence of $[CpM(CO)_3]_2$. The complex mixture of products formed by broad-band irradiation may result from secondary photoreactions caused by short wavelength light, for example CO loss from $CpMo(CO)_3Et$ [15] and Mo–In bond cleavage of $[CpMo(CO)_3]_xIn_{3-x}$ (see below).

The mechanism

The photochemistry of $[CpMo(CO)_3]_2$ has been studied extensively [16–19]. Depending upon the conditions—polarity of solvent, presence or absence of strongly-binding ligands, wavelength of light—CO loss and homolytic and heterolytic cleavage of the Mo–Mo bond have been reported. In the reactions described in this article it is assumed that the productive primary photoevent is homolytic Mo–Mo bond cleavage to form $CpMo(CO)_3$ radicals. CO loss seems unlikely, given the good yields of (tricarbonyl)molybdenum-containing products. Peripheral evidence that $CpMo(CO)_3$ radical (as distinct from $CpMo(CO)_3$ anion or cation) can react with trialkylindium compounds is provided by the rapid dark reaction between $InEt_3$ and "$[CpCr(CO)_3]_2$" (which exists in thermal equilibrium with its monomer radical [20]) although the products have not been identified. The rate of reaction of $CpMo(CO)_3$ radicals with $InEt_3$ must be rapid enough to compete with recombination of $CpMo(CO)_3$ radicals, given the high quantum yield for loss of $[CpMo(CO)_3]_2$ by Eq. 1a (0.40 ± 0.07 at 577 nm in benzene). At the same time the quantum yield is not so large as to demonstrate radical chain reactions. (Radical chains are important in the decomposition of other main-group organometallic compounds, e.g. alkylmercurials [21].)

The exact nature of the reaction between $CpMo(CO)_3$ and InR_3 is an important question. One plausible mechanism is β-H abstraction from an alkyl group of trialkylindium as in Eqs. 4, based solely on the observation that no reaction occurs for $InMe_3$ (without β hydrogens) but does occur for $InEt_3$ and $In(^tBu)_3$.

$$CpMo(CO)_3 + H\text{-}CH_2CH_2InEt_2 \rightarrow CpMo(CO)_3H + C_2H_4 + InEt_2 \qquad (4a)$$

$$CpMo(CO)_3H + InEt_3 \rightarrow C_2H_6 + CpMo(CO)_3InEt_2 \qquad (4b)$$

$$CpMo(CO)_3 + InEt_2 \rightarrow CpMo(CO)_3InEt_2 \qquad (4c)$$

Testing another trialkylindium compound without β hydrogens, trineopentylindium [22,23] was found to react with $[CpMo(CO)_3]_2$ under 577 nm photolysis. Its rate of reaction is much less than that of $InEt_3$, as indicated by the slower reaction and lower quantum yield (0.006). Still, this is proof that the reaction between InR_3 and $CpMo(CO)_3$ can proceed by some mechanism other than β-hydrogen abstraction. If there is a common single mechanism—which need not be the case—for all three reactive trialkylindium compounds and diethylzinc, the simplest mechanism is direct bimolecular radical substitution indicated in Eqs. 3. If so the sequence of reactivities observed (nonreactivity of $InMe_3$ and $ZnMe_2$, sluggish reactivity of $In(CH_2CMe_3)_3$, rapid reactions of $InEt_3$, $ZnEt_2$, and $In(CMe_3)_3$) is consistent with sequentially decreasing strengths of metal–alkyl bonds and/or increasing stabilities of the free radicals, as indicated by relative H–alkyl bond energies [25].

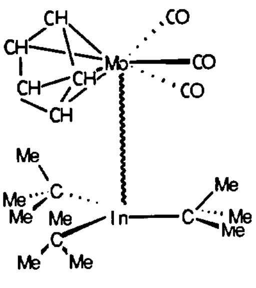
The most compelling direct evidence that this radical substitution mechanism (Eq. 3) does indeed operate for $InEt_3$ and $ZnEt_2$ is the formation of butane and $CpMo(CO)_3Et$, neither of which would be formed by the β-hydrogen abstraction mechanism of Eq. 4. In fact, for the $ZnEt_2 + [CpMo(CO)_3]_2$ photoreaction, approximately 25% of the reacting ethyl groups appear as $CpMo(CO)_3Et$, 30% as butane, and the remainder as ethylene and ethane. (In the $InEt_3$ reaction, butane is definitely present but its ^1H NMR signals overlap ethyl signals of $[CpMo(CO)_3]_xInEt_{3-x}$.) Thus at least half of the $ZnEt_2$ reaction must proceed by the radical mechanism analogous to Eq. 3.

A second line of evidence for radical reactions is that addition of dihydroanthracene to the photoreaction systems does not materially alter the reaction rate but does suppress the formation of ethylene (as well as butane and the Mo-ethyl compound) in favor of ethane. In order that it be suppressed by dihydroanthracene, a major route to formation of ethylene must be by decomposition of ethyl radical (Eq. 3b) and not by β-hydrogen abstraction (Eq. 4a). In the absence of $InEt_3$ and $ZnEt_2$, there is no photochemical reaction between dihydroanthracene and $[CpMo(CO)_3]_2$ at 577 nm.

Even direct bimolecular radical substitution may be more complicated than it appears in Eq. 3a. It is intriguing that InR_3 reacts so rapidly with $CpMo(CO)_3$; especially for $R = {}^tBu$ [14] it is difficult to imagine how a molybdenum-centered radical can attack the sterically encumbered indium center, as drawn in **1**. One alternative is long-range electron transfer, followed by fragmentation and rearrangement of the reaction complex. (For one example from Tl^{III} chemistry see Ref. 24, but note that Tl^{III} is a better oxidant than In^{III}.) Another alternative is attack of an oxygen-centered radical at the indium center (**2**), again followed by rearrangement to the Mo–In bonded species. The hypothetical transition state/intermediate drawn in **2** is suggested by the well-known affinity of organoindium compounds for oxygen donors, and more directly by its similarity to the known magnesium-$CpMo(CO)_3$ compound (**3**) [26], and several aluminum- and zirconocene-$CpMo(CO)_3$ compounds [5,27,28]. A third alternative is that $In({}^tBu)_3$ may indeed undergo β-hydrogen abstraction by $CpMo(CO)_3$, driven perhaps by statistics or unusually active β C–H bonds.

Thermodynamic considerations, and reactions of metallic indium

One important feature of organoindium compounds is that trialkylindium compounds are thermodynamically unstable, according to Eq. 5 [3,4,29]. But a similar situation does not necessarily hold for tri(transition-metal)indium compounds; the



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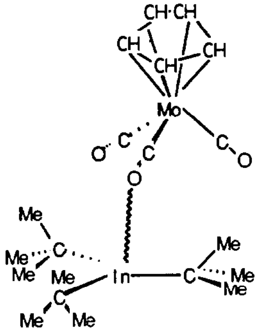

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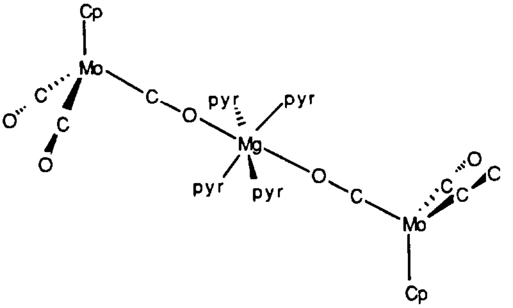

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transition metal analog of reaction 5, Eq. 6, might be endothermic and its reverse might occur.

$$InMe_3(s) \rightarrow In(s) + 3/2\ C_2H_6 \quad \Delta H = -59.5 \text{ kcal/mole} \qquad (5)$$

$$[CpMo(CO)_3]_3In \rightarrow In(s) + 3/2\ [CpMo(CO)_3]_2 \qquad (6)$$

No dark reaction in either direction was observed at room temperature but the reaction of Eq. 6 can be driven in either direction photochemically. By photolyzing at 577 nm $[CpMo(CO)_3]_2$ does react with metallic indium, previously deposited by UV photolysis of $In(^tBu)_3$ [14]. (Indium metal reacts thermally with mercuric- or thallium-transition metal bond-containing compounds; see Refs. 3, 4, 8, 30.) Thus there is the interesting opportunity to photochemically deposit an indium film from solution at one wavelength, and to redissolve it by photolysis at another wavelength. $[CpMo(CO)_3]_3In$ was the major product in photolyzed mixtures of $[CpMo(CO)_3]_2$ and metallic indium, but there were small amounts of other unidentified compounds. Photolysis of $[CpMo(CO)_3]_3In$ at 435 nm produces $[CpMo(CO)_3]_2$ and, presumably, metallic indium, although the reaction is not very efficient nor clean; the gray material suspended in photolyzed mixtures is assumed to be metallic indium but has not been fully characterized. Related photochemical reactions are known which release elemental Zn, Cd, Hg, or Tl from compounds with transition metals [31–34].

Equilibria among $[CpMo(CO)_3]_xInEt_{3-x}$*. Reconsideration*

The equilibria among $[CpMo(CO)_3]_xGaMe_{3-x}$ compounds and $GaMe_3$, and related exchange reactions among tungsten and/or thallium analogs, have been known for some time [5–7]. The exact mechanism by which this occurs has not been established, but in view of the observations reported in this study the exchange reaction cannot involve free $CpMo(CO)_3$ radicals (at least for molybdenum and ethylindium). Such radicals would react with the $InEt_3$ present in equilibrium amounts, and "$CpMo(CO)_3InEt_2$" would quickly consume itself. In fact, solutions of "$CpMo(CO_3)InEt_2$" are thermally stable once the exchange equilibria have been established, and no ethylene, butane, or $CpMo(CO)_3Et$ is formed (traces of ethane do form, presumably by adventitious hydrolysis). However, photolysis of these solutions (435 nm) does slowly form some ethylene, ethane, and $[CpMo(CO)_3]_2$ along with other unidentified products. Whether the photoactive species is the small equilibrium amount of $[CpMo(CO)_3]_3In$ (λ_{max} 382 nm in toluene) or $[CpMo(CO)_3]_2InEt$ or $CpMo(CO)_3InEt_2$ is unknown, as the photochemistry of $[CpMo(CO)_3]_xInEt_{3-x}$ at 435 nm is quite complicated and further elaboration has not been attempted.

Summary and conclusion

The rapid photoreaction of $[CpMo(CO)_3]_2$ with trialkylindium and dialkylzinc compounds is consistent with radical substitution chemistry, and the apparent ability of $CpMo(CO)_3$ radical to displace an alkyl radical from InR_3 reveals considerable strength for the $Cp(CO)_3Mo–In$ bond. This is demonstrated further by the photoreaction of $[CpMo(CO)_3]_2$ with metallic indium to form $[CpMo(CO)_3]_3In$.

One feature of the reaction, that it does not involve β-hydrogen abstraction (except perhaps for $In(^tBu)_3$) as the major reaction path, is quite intriguing. The benefit of using higher alkyl compounds (instead of methyl compounds) of the aluminum metals in MOCVD processes is sometimes ascribed to reactive β-hydrogen atoms. This may be true, given the high temperatures and complexity of the reactions occurring in the MOCVD reactor. But the present work illustrates examples where β-hydrogen atoms of indium-alkyl compounds are apparently unaffected even by free radicals in solution. This adds to the number of known examples [2–4] where reactive transition metal compounds—which in traditional organometallic lore have great affinity for β-hydrogen atoms—attack the In–C bonds of alkylindium compounds and leave their β C–H bonds alone.

Experimental

CAUTION: Alkylindium and alkylzinc compounds are very sensitive to oxygen and moisture, and often ignite spontaneously in air!

All reactions were carried out in an inert atmosphere, usually nitrogen in a drybox, and solvents were dried and degassed prior to use. $[CpMo(CO)_3]_2$, $InMe_3$, $InEt_3$, $ZnMe_2$, and $ZnEt_2$ were obtained commercially and used as received. $CpMo(CO)_3H$ [35], $In(^tBu)_3$ [14], and $In(CH_2CMe_3)_3$ [22,23] were prepared by modifications of published methods. The compounds $CpMo(CO)_3InR_2$ ($R = Et$, ^tBu, CH_2CMe_3) present in photolyzed reaction solutions were identified by comparison of their ^1H NMR spectra with standard samples prepared by the reaction between $CpMo(CO)_3H$ and InR_3, and between $[CpMo(CO)_3]_3In$ and InR_3 [3–7].

Table 1

^{1}H NMR data [a]

Compound	C_5H_5 resonance	Other resonances [b]
$[CpMo(CO)_3]_2$	4.65	
$CpMo(CO)_3InEt_2$	4.59 [c]	0.95 (br m), 1.40 (t, 8)
$[CpMo(CO)_3]_2InEt$	4.74 [d]	1.21 (q), 1.68 (t, 8)
$[CpMo(CO)_3]_3In$	4.97	
$CpMo(CO)_3In({}^tBu)_2$	4.75	1.39
$CpMo(CO)_3In(CH_2CMe_3)_2$	4.64	1.14, 1.45
$CpMo(CO)_3Et$	4.40	1.47 (pseudo q), 1.56 (pseudo t, 6)
$CpMo(CO)_3CH_2CMe_3$	4.41	1.16 (s, CH_3), 1.77 (s, CH_2)
$[CpMo(CO)_3]_2Zn$	4.67	
$CpMo(CO)_3ZnEt$	4.40	[e]
$InEt_3$		0.46 (q), 1.38 (t, 8)
$In({}^tBu)_3$		1.26
$In(CH_2CMe_3)_3$		1.02 (s, CH_2), 1.09 (s, CH_3)

[a] All compounds in C_6D_6 solution. All chemical shifts in ppm downfield from external Me_4Si. Spectra were recorded at ambient probe temperature using a GE QE-300 spectrometer. [b] Multiplicity, coupling constant (Hz), and assignment in parentheses. [c] Depending on concentration and/or amounts of excess $InEt_3$, this signal may appear from 4.56 to 4.62 ppm. [d] Only present in equilibrium with $CpMo(CO)_3InEt_2$. [e] Coincident with excess $ZnEt_2$ at 0.07 (q), 1.10 (t, 8).

The compound $CpMo(CO)_3InMe_2$ was obtained as a white crystalline solid from cold hexane solutions containing excess $InMe_3$, but the equilibrium reactions were sufficiently rapid even in the solid state at room temperature to form yellow/orange $[CpMo(CO)_3]_3In$ and $InMe_3$ after several hours. ^{1}H NMR parameters are listed in Table 1.

Photolyses were carried out using a 1000-watt Hg/Xe lamp. The output beam was filtered through 20 cm water, then through a 577 nm or 435 nm interference filter. For NMR studies the beam was focussed to ca. 1 cm^2 and the NMR sample was moved to expose all parts of the solution relatively uniformly. For quantitative quantum yield studies the beam was allowed to diverge to a diameter of about 25 cm and the sample was placed at the center, where the beam was effectively uniform across the sample surface.

Photolysis reactions

In a representative photolysis reaction involving an alkylindium compound, 0.012 g $[CpMo(CO)_3]_2$ and 0.01 g $InEt_3$ (Mo : In = 1 : 1) were mixed in C_6D_6 and photolyzed using the focussed filtered light beam (see above) until the red color had bleached, ca. 1 min. ^{1}H NMR analysis of the pale yellow-pink solution revealed $CpMo(CO)_3InEt_2$, $[CpMo(CO)_3]_2InEt$, $CpMo(CO)_3Et$ (see Table 2), together with C_2H_4(^{1}H NMR 5.22) and C_2H_6(^{1}H NMR 0.77). Butane signals were obscured by the ethyl signals of $[CpMo(CO)_3]_xIn_{3-x}$. The presence of butane was confirmed in a separate experiment by photolyzing a comparable solution in vacuum and condensing the volatile compounds (primarily $InEt_3$ and n-butane) into an attached NMR tube. Chromatographic analysis of the reaction solutions was not attempted; the very active In-alkyl groups react with traces of moisture or oxygen to form irreproducible amounts of additional organic products. Photolysis of solutions

Table 2

Product distributions for photolysis reactions [a]

Initial amount of $[CpMo(CO)_3]_2$ [b]	Initial amount of $InEt_3$ [b]	Ratio Mo : In	Fraction of $CpMo(CO_3)InEt_2$ [c]	Fraction of $[CpMo(CO)_3]_2InEt$ [c]	Fraction of $CpMo(CO)_3Et$ [c]
0.012 g	0.010 g	1 : 1	85%	5%	10%
0.012 g	0.020 g	1 : 2	88%	4%	8%
0.012 g	0.030 g	1 : 3	94%	2%	4%

[a] For the reactions of Eqs. 1a, b. [b] Dissolved in 1 mL C_6D_6. [c] Expressed as percentage of total $CpMo(CO)_3$ present.

containing different ratios of $[CpMo(CO)_3]_2$ and $InEt_3$ provided $CpMo(CO)_3InEt_2$, $[CpMo(CO)_3)]_2InEt$, and $CpMo(CO)_3Et$ in different ratios; see Table 2.

For a preparative-scale reaction, a benzene mixture of 0.13 g $InEt_3$ and 0.70 g $[CpMo(CO)_3]_2$ was photolyzed 10 h at 577 nm. The solvent was evaporated, the residue was dried in high vacuum and washed with pentane, leaving 0.48 g crude $[CpMo(CO)_3]_3In$ [8,9] (88% based on In). Recrystallization from benzene/pentane provided an analytically pure sample. Found: C, 34.14; H, 1.80. $C_{24}H_{15}O_9InMo_3$ calcd.: C, 33.91; H, 1.78%.

In a typical photolysis reaction involving diethylzinc, 0.018 g $[CpMo(CO)_3]_2$ and 0.010 g Et_2Zn in C_6D_6 were photolyzed until bleached (ca. 1 min). By ^1H NMR analysis the solution contained $[CpMo(CO)_3]_2Zn$ [10] (ca. 70% of cyclopentadiene intensity), $CpMo(CO)_3ZnEt$ (ca. 5% of Cp intensity), $CpMo(CO)_3Et$ (ca. 25% of Cp intensity), together with C_2H_4, C_2H_6, and C_4H_{10}. On a preparative scale, a benzene mixture of 0.16 g $ZnEt_2$ and 0.50 g $[CpMo(CO)_3]_2$ was photolyzed 1 h at 577 nm. The solvent was evaporated and the residue was dried in high vacuum and washed with pentane, leaving 0.25 g crude $[CpMo(CO)_3]_2Zn$ [10] (88% based on Mo, assuming a stoichiometry $2\ [CpMo(CO)_3]_2 + ZnEt_2 \rightarrow 2\ CpMo(CO)_3Et + [CpMo(CO)_3]_2Zn$). Recrystallization from toluene provided an analytically pure sample. Found: C, 34.55; H, 1.95. $C_{16}H_{10}O_6Mo_2Zn_1$ calcd.: C, 34.60; H, 1.81%.

Quantum yield determination

In obtaining quantum yield information for these photoreactions, the procedure used is illustrated by the following example. A standard 3 mL air-tight cuvette was loaded with a stirred benzene solution of $[CpMo(CO)_3]_2$ (ca. 8.2×10^{-4} *M*) and excess triethylindium (20 μL). The absorbance of the solution before photolysis was 0.375 at 577 nm. The solution was then photolyzed in 5-second intervals and the absorbance measured after each interval. The rate of disappearance of $[CpMo(CO)_3]_2$ ("M_2") is governed by Eq. 7, which becomes Eq. 8 after using Beer's Law. Integrating Eq. 8 provides Eq. 9, where $A(t)$ is the solution absorbance at time t, B is a constant of integration, and $c = \phi_{eff} \times \epsilon \times b \times I \times 2.303/V$ (b = path length, I = light intensity in einstein/s, V = cell volume). (Note equivalence between present Eqs. 7, 8 and Eq. 1.9 of Ref. 36.) Equations 7–9 are strictly valid only if M_2 is the only absorbing species. However, Eq. 9 can be used in cases where there are small and relatively constant quantities of other absorbing species, provided the observed absorbance is corrected for their presence.

$$d[M_2]/dt = -(\phi_{eff} \times I/V) \times (1 - \exp(-2.303A)) \tag{7}$$

$$dA/dt = -(\phi_{eff} \times I \times \epsilon \times b/V) \times (1 - \exp(-2.303A)) \tag{8}$$

$$A(t) = (1/2.303) \times \ln(1 + B \times \exp(-ct)) \tag{9}$$

Fitting the measured absorbances (corrected for small amounts of residual absorbance) according to Eq. 9 provided a value for c of 0.0459(3) s^{-1}. The maximum difference between observed and fit absorbance values was 0.003, and the average 0.001. Repeating the procedure but using 5 μL of triethylindium gave a c of 0.0450(4). Calibration reactions, using CCl_4 [16] (5 and 20 μL) and no triethylindium, provided values for c of 0.032(2) and 0.049(1). Fitting the CCl_4 data to Eq. 9 is of questionable validity, owing to significant residual absorbance of unknown origin. This was especially troublesome when neat CCl_4 was used, for which a c value of 0.0313(7) was obtained. Still, the ratios of c values, corrected for different extinction coefficients and assuming a constant light intensity at the cuvette surface (I, in einstein/s), should give reasonable estimates for the ratio of effective quantum yields (average 1.16). Using the literature value of 0.35 for the absolute quantum yield for reaction with CCl_4 [16], the absolute quantum yield of 0.40 ± 0.07 is obtained for the triethylindium reaction. The rates of photoreaction of $ZnEt_2$ and $In(CH_2CMe_3)_3$ were measured similarly, and relative quantum yields (1.0 and 0.014 respectively) were computed against the $InEt_3$ photoreaction rate.

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