a variable temperature probe. ^{13}C NMR were recorded on a Varian XL-100 instrument fitted with a broad band decompling and variable temperature probe.

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Registry No.—Benzene, 71-43-2; toluene, 108-88-3; anisole, 100-66-3; fluorobenzene, 462-06-6; *m*-xylene, 108-38-3; *p*-methylanisole, 104-93-8; mesitylene, 108-67-8; 1,3,5-trimethoxybenzene, 621-23-8; 1,2,4-trimethoxybenzene, 135-77-3; 1,2,3,4,5-pentamethylbenzene, 700-12-9; mercuric trifluoroacetate, 13257-51-7; methylmercury acetate, 108-07-6; fluorosulfuric acid, 7789-21-1.

Supplementary Material Available. ^1H NMR spectra of anisole- and *m*-xylenemercurinium ions and ^{13}C NMR spectra of fluorobenzene- and anisolemercurinium ions (4 pages). For simplicity signals due to the counteranion were deleted. Ordering information is given on any current masthead page.

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Consecutive Decomposition Modes for *m*-Trifluoromethylphenylcopper in Ether[1]

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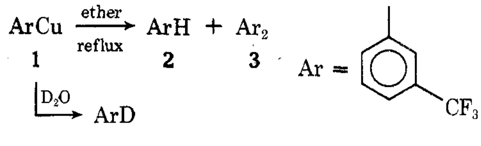
The decomposition of *m*-trifluoromethylphenylcopper in refluxing ether, both in the absence and presence of benzalacetophenone, has been monitored by withdrawing samples from time to time and quenching with D_2O. During the first phase of the decomposition, 3,3′-bis(trifluoromethyl)biphenyl (biaryl) is produced in both cases and, in the presence of the enone, conjugate addition occurs as well; this is the first reported case of a simple conjugate addition of an organocopper in the absence of lithium or magnesium salts. When approximately one-half of the organocopper has been consumed, the above behavior ceases and the remainder of the organocopper is converted to benzotrifluoride by removal of hydrogen from the solvent; such hydrogen removal was demonstrated by performing the decomposition in perdeuteriotetrahydrofuran and noting that the benzotrifluoride produced was monodeuterated to the extent of 46%. It is believed that the organocopper exists in these solvents as a cluster compound which splits out aryl groups pairwise, in competition with conjugate addition, until an intermediate such as Ar_4Cu_8 is reached; the latter then reacts with solvent by one of a number of possible mechanisms, which are discussed.

Results

While attempting to study one aspect of the mechanism of the Ullmann biaryl synthesis,[2] we made the intriguing observation that during the course of decomposition of *m*-trifluoromethylphenylcopper (1)[3] in ether solvents, the nature of the process changes markedly from the beginning to the end of the reaction. If this decomposition is carried out in refluxing ether and samples are withdrawn and quenched with water at various times, the quantities of benzotrifluoride (**2**, arene) in the quenched samples decrease and those of 3,3′-bis(trifluoromethyl)biphenyl (**3**, biaryl) increase until after about 6 h when the quantities of the two compounds cease changing.

However, it was soon found that those deceptively simple results mask quite surprising changes in the course of the reaction which start at about the time the quantities of products in the quenched samples become constant. This was ascertained by repeating the reaction, quenching the withdrawn samples with D_2O, and determining the yields in the quenched samples of biaryl (**3**) and arene (**2**) as well as the deuterium content of the latter (by combined gas chromatography–mass spectrometry); this procedure allows a distinction to be made between benzotrifluoride (ArH) which is present in the unquenched sample and that (ArD) which arises upon quenching the reaction mixture, presumably by protonation of an organocopper compound.



The first three columns of Table I indicate the raw data from such an experiment. The zero hour sample was withdrawn as soon as possible after the ether solution of arylcopper (1) and the gas chromatographic standard, durene, was removed from the glove box[4] in which it was prepared and before heat was applied. It is again seen that during the interval between 5 and 20 h, the quantities of biaryl and arene in the quenched samples become constant but that a substantial percent of the arene is monodeuterated and is thus derived from unreacted arylcopper; that is to say, even though reaction appears to cease some time between 5 and 20 h, a large amount of the arylcopper is still present. The fourth column indicates that, although there are some fluctuations in our material balance, owing mainly to the difficulty in sampling a mixture that becomes heterogeneous after a few hours (see below), the

Table I. Decomposition of *m*-Trifluoromethylphenylcopper in Refluxing Ether[a]

	Quantities present in quenched samples, mmol[b]			Derived quantities, mmol		
Time, h	Ar_2[c]	Arene[d] (% D)	Total[e]	ArCu present	ArH present	Ar_2 formed[f]
0	0.08	1.56 (83)	1.72	1.29	0.27	0
2.5	0.22	1.50 (74)	1.94	1.11	0.39	0.14
5.0	0.40	0.91 (64)	1.71	0.58	0.33	0.32
20.0	0.57	0.84 (30)	1.98	0.25	0.59	0.49
47.5	0.54	0.89 (1)	1.97	0.01	0.88	0.46
77	0.53	0.95 (0)	2.01	0	0.95	0.45
120	0.55	0.93 (0)	2.03	0	0.93	0.47

[a] Solutions were prepared by dissolving 500 mg of *m*-trifluoromethylphenylcopper in 35 ml of ether. [b] Quantities determined by gas chromatography utilizing as an internal standard durene, which was present during the reaction. [c] Ar = *m*-$CF_3C_6H_4$. [d] Benzotrifluoride. [e] mmol arene + 2 (mmol biaryl). [f] After the zero time sample was withdrawn.

total quantity of aryl groups accounted for remains reasonably constant. The quantity of arylcopper present at each time is simply derived by multiplying the total quantity of arene in the quenched samples by the fraction ArD; these quantities are in the fifth column of Table I. The quantity of arene which is present at any time in the reaction mixture before quenching is then the total arene after quenching minus the quantity of arylcopper present and these quantities are in column 6. In the last column, the yields of biaryl (**3**) at various times are listed; they are calculated by subtracting the small quantity (0.08 mmol) of biaryl which is present as a contaminant when the arylcopper is first dissolved in the ether from the quantity of biaryl present at each time. Some arene (0.27 mmol) is present soon after the arylcopper is dissolved in the ether; a part of this may have been present as a contaminant in our sample of arylcopper, which was somewhat tacky, and the remainder may be formed by protolysis of the arylcopper by traces of moisture in the system.

The most striking feature of Table I is the fact that the formation of biaryl essentially ceases some time between 5 and 20 h, long before all of the arylcopper is consumed. The remaining arylcopper is thenceforth converted slowly to arene (**2**).

Organocopper(I) compounds frequently add to enones[5-7] although attempts to add 1 mol of an arylcopper to an enone in the absence of lithium or magnesium halides have heretofore resulted in failure.[5,6,8-10] Nevertheless, we have found that *m*-trifluoromethylphenylcopper does add to an excess of benzalacetophenone in ether solution in competition with self-coupling. When this reaction was monitored as in the previous case, the reaction course was found to be quite analogous to that without added benzalacetophenone. The results of this experiment (Table II), and two similar ones (one of them using aqueous DCl instead of D_2O alone as the quench), which exhibited the same behavior pattern, clearly indicate that conventional organocopper behavior is manifested for less than 20 h; that is to say, the yields of biaryl and conjugate addition product (**4**) remain constant after 20 h. On the other hand, unconventional behavior, the conversion to arene, does not occur to any appreciable extent until toward the end of the 20-h interval, but this reaction is essentially the only one undergone by the organocopper after 20 h. Furthermore, at the end of 20.5 h, the biaryl (**3**) and benzalacetophenone addition product (**4**) account for almost one-half of the 1.53 mmol of arylcopper present at time zero (2 × 0.25 mmol of biaryl + 0.21 mmol of addition product = 0.71 mmol).

$$\underset{\mathbf{1}}{\mathrm{ArCu}} + \mathrm{PhCH{=}CHCOPh} \xrightarrow{\text{ether}} \underset{\mathbf{2}}{\mathrm{ArH}} + \underset{\mathbf{3}}{\mathrm{Ar_2}} + \underset{\mathbf{4}}{\mathrm{Ph(Ar)CH{-}CH_2COPh}}$$

Since completely deuterated diethyl ether was unavailable to us, the source of the hydrogen which replaces the metal was probed by performing the decomposition of *m*-trifluoromethylphenylcopper (**1**) in refluxing perdeuteriotetrahydrofuran. Preliminary experiments in undeuterated THF using D_2O quenches established that at this higher temperature, the reaction proceeded more rapidly and that the final ratio (0.34) of arene to biaryl was far lower than that (1.7) in the ether experiment, but that the broad features of the reaction were the same; biaryl production virtually ceased before the arylcopper was consumed and after that point arene production was essentially the only reaction occurring. Because of the expense of perdeuteriotetrahydrofuran, the decomposition was performed on a far smaller scale than those in the above experiments and the solution was more concentrated. After the organometallic had been dissolved in the solvent and the solution removed from the glove box, a sample was withdrawn and quenched with D_2O to produce benzotrifluoride (**2**) with an ArD content of 76%; thus, the quantity of benzotrifluoride present at zero time was somewhat higher than those of the previous experiments (for example, in a small-scale experiment in THF, 90% of the arene produced upon quenching the zero time sample with D_2O was monodeuterated; see also Tables I and II); this is probably due to the presence of more moisture in the labeled THF which was used directly from the ampule in which it was supplied. The reaction was followed by quenching withdrawn samples with H_2O. The ArD content of the benzotrifluoride produced when reaction was complete was 46%. Although the small quantities used in this experiment precluded an accurate estimate of the

Table II. Decomposition of *m*-Trifluoromethylphenylcopper in the Presence of Benzalacetophenone in Refluxing Ether[a]

	Compounds present in quenched samples, mmol[b]				Derived quantities, mmol		
Time, h	Ar_2[c]	Arene[d] (% D)	Addn product[e]	Total[f]	ArCu present	ArH present	Ar_2 formed[g]
0	0.08	1.79 (85)	0	1.95	1.53	0.26	0
2.5	0.17	1.36 (81)	0.13	1.82	1.10	0.25	0.09
5.0	0.25	1.04 (78)	0.17	1.71	0.81	0.23	0.17
20.5	0.33	0.82 (66)	0.21	1.69	0.54	0.28	0.25
46	0.34	0.80 (30)	0.22	1.70	0.24	0.56	0.26
79	0.34	0.85 (2)	0.20	1.73	0.02	0.83	0.26
116	0.31	0.68 (0)[h]	0.23	1.53	0	0.68[h]	0.23

[a-d] As in Table I. [e] 1,3-Diphenyl-3-(*m*-trifluoromethylphenyl)propanone (**4**). [f] mmol arene + mmol **4** + 2 (mmol biaryl). [g] After the zero time sample was withdrawn. [h] Arene lost owing to evaporation during the long heating period.

percent conversion to benzotrifluoride of the arylcopper present at time zero, one can be confident that most, if not all, of the benzotrifluoride produced after time zero resulted from deuterium transfer from the solvent to the aryl groups since the 54% of undeuterated arene present at the end of the reaction can easily be accounted for as that which was present at time zero, presumably from hydrolysis of the organocopper. In fact, it can be calculated that if the percent conversion to arene of arylcopper present at time zero in the labeled THF were the same as that (10.4%) in the large scale more dilute run using predried THF, the percent ArD in the benzotrifluoride would be only 25%;[11] it thus appears that somewhat more arene and less biaryl result from decomposition of the arylcopper in the isotopic experiment.

Some interesting visual observations were made during the course of all the reactions described above. The original brownish black solution turned green after about 2 h (in the ether runs) and, after about 1 h further, copper plating was observed. After about 2 h more, a brown precipitate began to form.

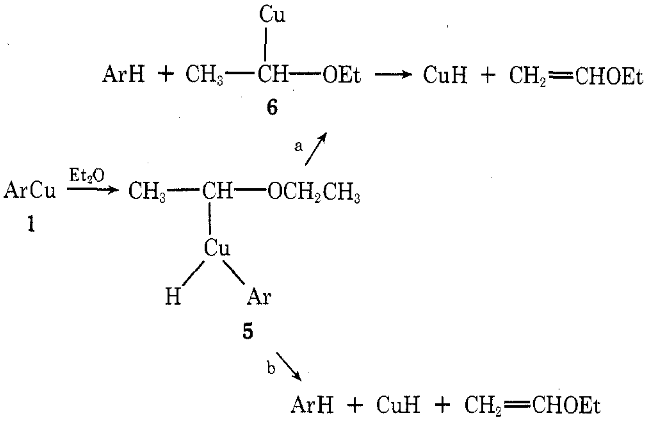
Discussion

As part of their elegant work on the structures and self-coupling reactions of fluorinated arylcoppers, Cairncross and Sheppard[3] made the fascinating observation that *m*-trifluoromethylphenylcopper (**1**), which is octameric in benzene solution, undergoes pairwise loss of aryl groups in the form of biaryl (**3**) and that metallic copper does not appear until about one-half of the arylcopper is decomposed to biaryl. Furthermore, they were able to isolate the green intermediate Ar_6Cu_8. Eventually, virtually all of the arylcopper is converted to biaryl.

$$Ar_8Cu_8 \longrightarrow Ar_2 + Ar_6Cu_8 \longrightarrow Ar_2 + Ar_4Cu_8 \longrightarrow 2Ar_2 + 8Cu$$

Their discovery provides an excellent basis for a rationalization of our own otherwise bewildering results. It appears likely that the cluster compound which exists in ether also splits out biaryl stepwise in competition with adding to benzalacetophenone, when the latter is present. However, some intermediate, present when about one-half of the aryl groups have been consumed (Ar_4Cu_8 if the original compound is octameric in ether), decomposes in a different way to yield arene by interaction with the solvent. The green color which develops fairly early in our decomposition reactions may very well correspond to the complex Ar_6Cu_8 isolated by Cairncross and Sheppard.[3] This finding is a rather remarkable demonstration of the different behavior of which arylcoppers in different states are capable and it suggests possibly interesting properties or organocopper compounds in which the average oxidation level of the metal is between 0 and 1.

Four different general modes of transfer of hydrogen from the ether solvent to the aryl group can be envisioned. (1) A proton abstraction by the arylcopper appears somewhat unlikely in view of the finding by Whitesides (footnote 21 of ref 12) that alkylcoppers are not sufficiently basic to abstract protons from diethyl ether; alkylcoppers would be expected to be far more basic than arylcoppers. However, this route cannot be completely ruled out since our present state of knowledge about species such as Ar_4Cu_8 is negligible. (2) Abstraction of hydrogen from the ether by nascent copper and subsequent reaction of the copper hydride with the arylcopper. An analogy for the last step is available from the work of Whitesides et al. on the decomposition of alkylcoppers.[13] However, we know of no precedents in copper chemistry for the hydrogen removal step, although Tamura and Kochi,[14] in order to account for the production of excess alkane during decomposition of alkylmanganese compounds, have speculated that an active form of manganese may be capable of dehydrogenating THF to form a manganese hydride. (3) An oxidative addition of a CH bond of the ether to the arylcopper(I) could provide an arylcopper(III) hydride (**5**) which, by reductive elimination (path a), could yield arene and an organocopper (**6**).[15,16] Another mole of arene would then be produced by reaction of the arylcopper with copper hydride which would readily be lost from **6**. Alternatively, the same products could be formed from **5** by heterolytic cleavage of the bond between the ether moiety and copper (path b) with either concerted abstraction of the β proton by the aryl group (oxidative elimination[17]) or formation of a carbonium ion (oxidative solvolysis[17]) and subsequent abstraction of the β proton. The oxidative addition of alkyl and aryl CH bonds to various transition metals has ample precedent.[18] (4) The form of organocopper present during the latter part of the reaction may decompose to aryl radicals which can abstract hydrogen atoms from the ether. The α-CH bonds of ethers are quite labile toward hydrogen atom removal.[19] While Cairncross and Sheppard[3] found no evidence for attack of aryl radicals on the benzene solvent during the decomposition of *m*-trifluoromethylphenylcopper, it may be either that coordination of ether with the organometallic changes the reactivity pattern or that the formation of radicals is reversible and that if no particularly low energy reaction path is available to the aryl radicals, they recombine with copper leading eventually to biaryl. A number of examples are available of radical decomposition of alkylcoppers and in several cases the alkyl radicals remove hydrogen atoms from the ether solvent;[20] this mode of decomposition is particularly prevalent in the case of alkylcoppers lacking β-hydrogen atoms, although the possibility has recently been raised that alkylcoppers in general may decompose by a radical pathway.[21] The radical pathway 4 has the best precedents but pathway 3 is more consistent with the apparent absence of aryl radicals during the decomposition of **1** in benzene.



In summary, a cluster compound of *m*-trifluoromethylphenylcopper appears to lose aryl groups by self-coupling and by conjugate addition to an enone until an intermediate species is reached. The latter organometallic does not undergo the above reactions but instead a hydrogen of the ether solvent replaces the copper to form benzotrifluoride; further work would be required to elucidate the nature of this latter reaction. This work provides the first example of the simple conjugate addition of an organocopper in the absence of lithium or magnesium salts.

Experimental Section

General. Routine infrared spectra were taken on a Beckman IR-8 spectrophotometer; when spectra were needed below 625 cm^{-1}, a Beckman IR-10 or IR-12 spectrophotometer was used. Nuclear magnetic resonance spectra were determined on a Varian T-60 spectrometer. Chemical shift data are reported in δ (ppm) units relative to tetramethylsilane. For purity checks on deuterated reagents, weighed amounts of 1,4-dioxane or chloroform were used as appropriate standards. Mass spectra were recorded on a LKB-9000 combined gas chromatograph–mass spectrometer; high-resolution mass spectra were determined on an AEI MS-9 spectrometer using a direct insertion probe at 70 eV.

Gas–liquid partition chromatographic (GLC) analyses were performed on a Hewlett-Packard 5750 gas chromatograph using a Disc Instruments No. 229 Series D Disc chart integrator or on a Varian Aerograph 1860-3 gas chromatograph with a No. 204 Disc chart integrator. These instruments were equipped with flame ionization detectors. Stainless steel columns (10 ft × 0.125 in.) were used. The flow rate of air was approximately 360 ml/min and of hydrogen about 52 ml/min; nitrogen carrier gas flow rates (ml/min) were 50 for the 3% OV-17 on 100/120 mesh Gas Chrom Q (column A), 22 for the 10% Carbowax 20M on 60/80 mesh Chromosorb W (B), and 47 for the 3% OV-225 on 100/120 mesh Gas Chrom Q (C). Absolute yields were calculated from peak areas using durene as internal standard. Calibration curves of three points were constructed utilizing flame response factors obtained with authentic samples. The identities of all reaction products of which authentic samples were available were checked by comparison of their retention times by coinjection on two GLC columns as well as of their mass spectra.

The percent of monodeuteriobenzotrifluoride in labeled samples of arene was determined from the relative peak heights[22] in the combined GLC–mass spectrogram at 15 eV utilizing column B.

Drybox work was performed in a Labconco fiberglass controlled atmosphere glove box. The prepurified nitrogen was passed through a tube of copper turnings, heated (450 °C) in a tube furnace, and a column of Drierite. The usual precautions for handling air and moisture sensitive organometallic compounds were observed.[23] The apparatus in which the organocopper was used was assembled and charged with the reagents in the glove box and was then removed to the bench where the dry nitrogen atmosphere was maintained.

Reagents and Solvents. Durene, *m*-iodobenzotrifluoride, magnesium, and tetrahydrofuran-d_8 (Norell Chemical Co.) were used directly as obtained from commercial sources. *m*-Bromobenzotrifluoride (Pierce Chemical Co.) was also used as supplied; it is known to contain ca. 2% of the para isomer which cannot be removed by distillation through a spinning band column.[26] Benzalacetophenone (chalcone, Eastman and J. T. Baker) was recrystallized from ethanol, mp 59.0–59.5 °C. Copper powder (Valimet 1107, formerly Englehard Magna 1107) was activated[28] with 0.24 M aqueous ammonia. 1,4-Dioxane was heated at reflux over lithium aluminum hydride, distilled at 101 °C, and stored under nitrogen over 5A molecular sieves. Deuterium chloride solution was prepared by adding deuterium oxide to benzoyl chloride (1:2 mole ratio) and distilling under nitrogen. Deuterium oxide-d_2 (Stohler Isotope Chemicals, 99.8% D) purity checks (NMR vs. dioxane standard) were performed on various bottles and ranged from 99.2 to 99.9% D. Diethyl ether (J. T. Baker, anhydrous reagent), was heated at reflux over lithium aluminum hydride for several hours and distilled under nitrogen. Tetrahydrofuran (Fisher certified) was heated at reflux with lithium aluminum hydride for several hours, distilled under nitrogen, bp 66 °C, and stored in the drybox for use in organocopper reactions.

3,3′-Bis(trifluoromethyl)biphenyl (3). This compound was prepared by an Ullmann coupling of *m*-iodobenzotrifluoride according to the procedure of Petit and Tatlow.[24] The product distilled at atmospheric pressure at 242.0–243.5 °C (lit.[24] bp 237–240 °C). GLC analysis indicated greater than 99% purity: NMR (CCl_4) 7.5–7.8 ppm (m); ir 1343, 1325, 1306, 1253, 1168, 1130, 1099, 1078, 1047, 795, and 702 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 291 [16, $(P + 1)^+$], 290 (base, P^+), 271 (15, $P^+ - F$), 207 (20), 206 (19), 205 (21), 179 (68), 177 (72), 145 (8, $C_{14}H_8F_6{}^{2+}$ or $C_7H_4F_3{}^+$), 99 (11), 74 (13), 59 (20).

3-(*m*-Trifluoromethylphenyl)-3-phenylpropiophenone (4). This compound was prepared by the method used by Holmberg and Axberg[25] to prepare 3,3-diphenylpropiophenone. A solution of 5.20 g (25.0 mmol) of benzalacetophenone in dry ether (40 ml) was added dropwise during 50 min to the Grignard reagent prepared from 1.41 g (62.5 mmol) of *m*-bromobenzotrifluoride, and 1.50 g (61.8 mmol) of magnesium in 30 ml of dry ether. The addition rate was controlled so as to maintain the mixture at reflux (34–36 °C) and the mixture was heated at reflux for an additional 20 min. The reaction products were poured into a mixture of ice water and hydrochloric acid and the resulting mixture was extracted with ether. The ether extract was washed with saturated solutions of sodium bicarbonate and sodium chloride. Concentration of the dried ether extract gave a brown oil which was twice recrystallized from ethanol–benzene (5:3) to give a tan solid: mp 60.7–62.0 °C; ir (CCl_4) 3100–3030 (ArCH), 1690 (C=O), 1330 (CF_3), 1130 cm^{-1}; NMR (CCl_4) δ 6.8 (m, ArH), 4.9 (t, CH), and 3.7 ppm (d, CH_2); mass spectrum (70 eV) *m/e* (rel intensity) 354 (24, P^+), 336 (11), 335 (10, $P^+ - F$), 236 (10), 235 (63, $C_6H_5C^+HC_6H_4CF_3$), 171 (10), 166 (16), 165 (23), 106 (25), 105 (base, $C_6H_5CO^+$), 77 (80, $C_6H_5{}^+$), 51 (10); high-resolution mass spectrometric molecular weight calcd for $C_{22}H_{17}F_3O$, 354.1231; found, 354.1224.

***m*-Trifluoromethylphenylcopper (1).** The compound was prepared according to the method of Cairncross and Sheppard.[3,26] A four-neck 100-ml round-bottom flask was fitted with a condenser with nitrogen inlet, a thermometer, a dropping funnel with pressure equalizing arm, and a filtering assembly consisting of a medium sintered glass filter followed by an adapter to a vacuum stopcock leading to a one-neck O-ring receiving flask.

After magnesium (0.97 g, 40 mmol) had been charged to the flask, the oven-dried assembled apparatus was further dried by flame while being purged with nitrogen; a solution of 9.0 g (40 mmol) of *m*-bromobenzotrifluoride in 40 ml of anhydrous distilled ether was added dropwise during 0.5–0.75 h to the magnesium with magnetic stirring at a rate which allowed the mixture to reflux gently. The mixture was heated at reflux for a total time of 1 h from the start of the addition and then cooled to 0 °C. A solid addition tube containing 6.3 g (44 mmol) of purified copper(I) bromide[27] was substituted for the thermometer under increased nitrogen flow; the contents were added in portions in a few minutes. After being stirred for 0.5 h at 0 °C, the mixture was slowly treated over 0.75 h with 15 ml of dry distilled dioxane, and enough cold ether was added to fill the flask (ca. 40 ml). The mixture was filtered in vacuo by inverting the entire apparatus while the filter assembly and receiving flask were being cooled. The solid was washed with an ice-cold solution of ether (40 ml) and dioxane (5 ml) in three portions over 1–1.5 h.

The filtrate was evaporated first on a flash evaporator using a Sargent-Welch Duo-Seal pump (no. 1399) with two traps in Dewar flasks filled with liquid nitrogen. When the distillation flask was cooled in slush baths of 2-propanol/dry ice and 1,2-dichloroethane/liquid nitrogen (−35°), 0.6–2.0 mm pressure was obtained and the bulk of the solvent was stripped off in 3–4 h. The last 10 ml of solvent, including dioxane, was removed on a vacuum line at ca. 10^{-5} mm using successively the above two slushes followed by an ice bath for 4 h to yield a sticky, brownish black solid. The evacuated flask was taken into the glove box and the contents packed as weighed samples (usually 0.50 g) in vials sealed with Parafilm and stored in a closed jar in a Dewar flask of dry ice. Samples were removed for use singly by removing a vial from the jar in a nitrogen-filled glove bag, then quickly returning the jar of samples to the Dewar. The best yield was 52% but not all the mass of solid could be scraped from the flask. The product was characterized and its purity determined in the following manner. A sample of *m*-trifluoromethylphenylcopper, which had been stored (−78 °C) for 6 months, was dissolved in dry ether and treated with deuterium oxide in a glove bag under nitrogen. The dried ether extract was analyzed by combined GLC–mass spectrometry. By far the major peak was deuteriobenzotrifluoride: MS (15 eV) *m/e* 148 (7.7), 147 (base, $DC_6H_4CF_3{}^+$), 146 (7.7). The arene was calculated[22] to be 98% monodeuterated. The gas chromatogram also showed that the arylcopper was contaminated with a few percent of dioxane, and minute traces of *m*-bromobenzotrifluoride, a chlorobenzotrifluoride, and biaryl; all were identified by mass spectrometry.

Some dry *m*-$CF_3C_6H_4Cu$ was exposed to air upon which the brownish black solid was transformed to green crystals. Anal. (Alfred Bernhardt) Cu, 36.03; Mg, 0.0 (limit 0.2%). The Cu/Mg atomic ratio is at least 70/1; Cairncross[26a] found 101/1, 117/1.

The infrared spectrum of 1 in the 2000–200-cm^{-1} region was determined as follows. By the use of Nujol which had been deoxygenated by passing nitrogen through it, a sample of $(m\text{-}CF_3C_6H_4)_8Cu_8$ of known high purity was mulled in a glove box between KBr plates; the edges of the plates were wrapped with Parafilm. The sample was placed in a desiccator along with a sample mulled between polypropylene plates similarly wrapped. The spectra of both samples were determined as soon as possible with a nitrogen atmosphere in the sample compartment. The polypropylene plates were used in the ranges 95–260 cm^{-1} (Beckman IR-11) and 200–400 cm^{-1} (Beckman IR-12); the KBr plates were used in the range 400–2000 cm^{-1} (Beckman IR-12). Spectrum: 1583 (m), 1456 (s), 1446 (sh), 1366 (m), 1348 (sh), 1324 (s), 1309 (s), 1179 (sh), 1140 (s,br), 1130 (sh), 1095 (s), 1082 (s), 1049 (s), 992 (m), 933 (m), 897 (m), 892 (m), 878 (m), 874 (sh), 864 (sh), 797 (s), 706 (m), 678 (s), 666 (m), 642 (m), 614 (m), 344, 278 cm^{-1}.

Decomposition of *m*-Trifluoromethylphenylcopper in the Absence and Presence of Benzalacetophenone in Ether. Initial exploratory experiments were performed with solutions of the organocopper and benzalacetophenone in ether. Samples were withdrawn from time to time and quenched with H_2O or D_2O. The final quantitative reactions were performed as follows. In a glove box, a 50-ml three-neck flask equipped with a serum cap, a condenser mounted with a gas inlet tube containing a stopcock, and, in those experiments with benzalacetophenone, an addition funnel was charged with 500 mg (2.40 mmol) of 1 and a solution of 67.2 mg (0.500 mmol) of durene in 35 ml of ether. The flask was removed from the glove box but maintained under a nitrogen atmosphere, magnetic stirring was started, and the first 1.5-ml sample was withdrawn by syringe through the septum. The solution was heated to reflux, when the timing began. Other 1.5-ml samples were withdrawn from time to time. Each sample was injected into 2 ml of ice-cold D_2O, and the mixture was stirred for 15 min under nitrogen and extracted with four 6–8-ml portions of ether. The dried (magnesium sulfate) ether extract was stored in capped vials at −20 °C within a closed jar containing Drierite. The visually observed changes which occurred during the reaction are described in the Results. The same procedure was used for the decompositions in the presence of benzalacetophenone, except that an ethereal solution of 2.00 g (9.60 mmol) of the latter was added by the addition funnel; the total volume of ether was also 35 ml. The experiment was done in triplicate; in one run, DCl in D_2O was used for the quench and it was necessary to wash the ether extracts with aqueous sodium bicarbonate and saturated saline solution before drying.

Decomposition of 1 in Tetrahydrofuran. The large-scale run was performed in the same manner as that in ether except that 35 ml of THF was used instead of the ether. The zero hour sample contained 0.10 mmol of biaryl and 1.98 mmol of arene which contained 92% ArD. The following are the results of analyses of samples withdrawn at the stated times after refluxing commenced [time, mmol of biaryl, mmol of arene (% ArD)]: 0.5 h, 0.24, 1.57 (89%); 1.5 h, 0.49, 1.33 (85%); 3 h, 0.97, 0.35 (41%); 18.5 h, 1.01, 0.31 (0%); 45 h, 1.05, 0.34 (0%). The small-scale runs in THF and perdeuterio-THF were performed in similar fashion except that 27 mg (0.20 mmol) of durene, 100 mg (0.48 mmol) of arylcopper, and 2 g of THF were used. In the experiment with unlabeled solvent, D_2O quenches were used. In the experiment with labeled solvent, the zero hour sample (0.3 ml) was quenched with D_2O and subsequent samples with H_2O. Extractions of the quenched samples were performed in centrifuge tubes, with centrifugation being used to break the emulsions. The yields of products were somewhat erratic but, in general, the usual trends were observed. In the labeled case, the zero hour sample contained arene which was 76% monodeuterated and the 3-, 5.5-, and 18-h samples were 43, 46, and 46% monodeuterated, respectively.

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Registry No.—1, 18206-44-5; 3, 580-82-5; 4, 58540-91-3; benzalacetophenone, 94-41-7; ether, 60-29-7.

References and Notes

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Methanolysis Products of Dichloro(1,5-cyclooctadiene)palladium(II) in the Presence of Bases and of Its Methoxy Adducts[1]

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When di-μ-chloro- and di-μ-methoxidobis(2-methoxycyclooct-5-enyl)dipalladium(II) were refluxed in methanol with and without added bases and when dichloro(1,5-cyclooctadiene)palladium(II) was refluxed in methanol with added bases, complex mixtures of products were obtained comprising 4-cyclooctenyl methyl ether and 2,4-, 2,5-, 3,5-, and 1,5-cyclooctadienyl methyl ethers as well as 4-cyclooctenone. Products were identified, and mechanisms are discussed.

Dichloro(1,5-cyclooctadiene)palladium(II) (1) and the methoxy adduct derived from it, di-μ-chlorobis(2-methoxycyclooct-5-enyl)dipalladium(II) (2-Cl), were reported by Chatt and Vallarino in 1957.[2] Although many other adducts of 1,5-cyclooctadiene have been made and some of their reactions studied,[3] the nature of the organic oxidation products has been given only scant attention.[4] In this report the complex mixtures of organic oxidation products formed when dichloro(1,5-