Decomplexation of Cyclopentadienylmanganese Tricarbonyls under Very Mild Conditions: A Novel Route to Substituted Cyclopentadienes and Their Application in Organometallic Synthesis

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Photolysis of cyclopentadienylmanganese tricarbonyl derivatives in the presence of a proton source leads to decomplexation and formation of the free cyclopentadiene in excellent yield. In contrast, attempted decomplexation using Ce(IV) or Fe(III) leads merely to decomposition products. It is proposed that, upon photolytic loss of a CO ligand, coordination of methanol or water facilitates an intramolecular proton transfer to the cyclopentadienyl ring. This method is applicable to polyfunctional molecules such as ethynylestradiol. In this new synthetic approach, these cymantrenes have also been used as precursors to the corresponding iron, tungsten, titanium, and rhenium complexes via the generation of the intermediate cyclopentadienes.

Introduction

Some years ago, we proposed a mild decomplexation method in the (arene)$Cr(CO)_3$ series, useful for synthetic purposes in organic chemistry.[1] The reaction, based on a photochemical oxidation in air and sunlight, at room temperature, produced quantitative amounts of substituted aromatics; since then this approach has been extensively developed.[2] Curiously, this idea has not been extrapolated to the metal cyclopentadienyl series, where the breaking of π-bonds, either chemically (e.g. with lithium on ferrocene)[3] or electrochemically,[4] leads to the formation of unstable cyclopentadienyls that are difficult to manipulate. It would be quite different if, during the liberation of the cyclopentadienide anion, the intermediate could be kept in a stable form: for example, as a neutral cyclopentadiene.

The cyclopentadienyl ligand, because of its size, robustness and electron count, is one of the most useful coordinating ligands in organometallic chemistry. Its almost ubiquitous nature has led to a plethora of articles on its functionalization,[5] such that metal cyclopentadienyls are now available with a wide variety of simple functional groups: alkyls,[6] silyls,[7] aryls,[8] formyls,[8] acids,[8] esters,[8] alcohols,[9] amines,[9] vinyls,[10] halogens,[11] sulfides,[12] phosphines,[13] and boryls.[14] Among the principal strategies employed are as follows: (i) the Friedel−Crafts reaction, whenever the organometallic substrate permits, which unfortunately is frequently not the case,[8c] (ii) an extension of Thiele's reaction,[15] which involves electrophilic attack on the nucleophilic cyclo-

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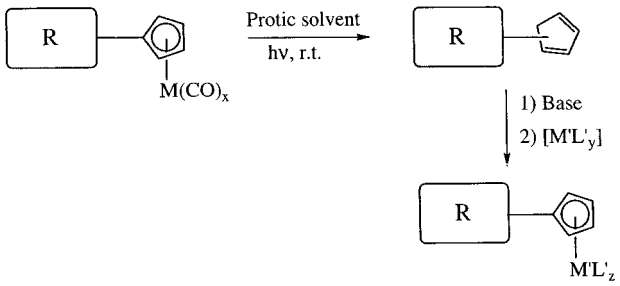
Scheme 1



pentadienides of sodium, lithium, or thallium,[8a,b] (iii) the action of bases on fulvenes[10,16] (iv) the action of nucleophiles on diazocyclopentadiene ($C_5H_4N_2$),[17] (v) the transformation of cyclopentenone,[9a,18] and (vi) the construction of substituted rings by means of various coupling methods.[6c,19] The variety of preparation methods utilized demonstrates both the absence of a dominant synthetic strategy suitable for all cases and the necessity of seeking new approaches to deal with novel problems.

We here describe a new synthetic approach that allows ready access to different families of cyclopentadienylmetal complexes whose substituents possess a degree of complexity compatible with the production of fine chemicals. Due to the therapeutic, analytical, or structural imperatives inherent in our bio-organometallic studies,[20] we chose to attempt to bind CpM fragments within complex biomolecules. These included the incorporation of $CpRe(CO)_3$ into hormones[21] or antibodies,[22] of CpFeCp′ or $CpCp'TiCl_2$ onto antitumoral agents,[23] and of $CpW(CO)_3R$ onto proteins.[24] In the particular case of radiopharmaceuticals possessing relatively short-lived isotopes, it is especially crucial that the synthetic routes be as rapid as possible and use the minimum number of steps.[17e,25]

In this context, the hypothetical transformations depicted in Scheme 1 require that several criteria be satisfied. First of all, the precursors must undergo mild and efficient decomplexation to generate the corresponding free cyclopentadiene.[26] In addition, the precursors should not only be readily prepared but also be sufficiently stable for easy handling and storage. In terms of the initial choice of organometallic system, it is clear that an easily oxidizable, carbonylated half-sandwich complex, $CpM(CO)_x$, is preferable to a sandwich molecule, CpMCp′, because of the ease of bond breaking, as well as simplification of the reaction and of the purification procedures. In view of the known relative instability and handling difficulties associated with $Cp'Co(CO)_2$ systems, we chose to focus our efforts on the $Cp'Mn(CO)_3$ (cymantrene) series of half-sandwiches which are stable in air but which can be conveniently oxidized when in solution.[30]

We have recently published our preliminary findings in this area[31] and now present the results of a more complete mechanistic and synthetic study, including the attachment of a number of organometallic fragments to molecular frameworks that exhibit estrogenic or antiestrogenic activity.

Results and Discussion

Synthetic Aspects. To test the viability of the approach, initial experiments were carried out using the propionylcymantrenes **1a**−**c** as precursors to the diarylalkenes **2a**−**c**. This latter type of skeleton, with OH instead of OMe groups, recognizes the estrogen receptor and shows a strong estrogenic effect, while with an $-O(CH_2)_3NMe_2$ chain in place of an OMe group, it becomes an antiestrogenic entity.[23b] A simple exchange of metals would thus permit changes in the properties (structure, cytotoxicity, radiopharmaceutical properties) of this system.

As shown in Scheme 2, McMurry coupling reactions between **1** and 4,4′-dimethoxybenzophenone yield the corresponding alkenes **2**. Molecule **1a** is itself easily obtained almost quantitatively by the Friedel−Crafts reaction between cymantrene and propionyl chloride in CS_2 in the presence of $AlCl_3$.[32] The Friedel−Crafts reaction with methylcymantrene gives two isomers, **1b**,**c**, which were separated by chromatography and identified by NMR. Heating an equimolar mixture of **1** and dimethoxybenzophenone in THF in the presence of the McMurry reagent $Zn/TiCl_4$[33] produced compounds **2a**−**c** in yields ranging from 85 to 50%. These complexes are yellow, stable in air in the solid state, and can be stored in the dark for several months with no trace of decomposition

Initial attempts to generate the free cyclopentadienes derived from **2** focused on chemical oxidation methods.

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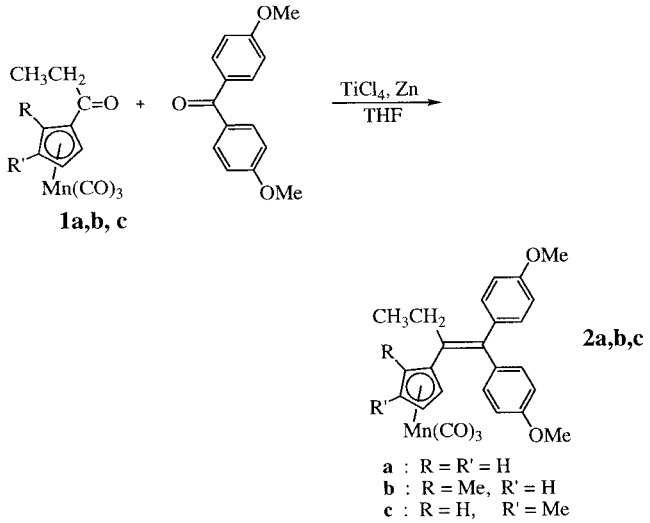
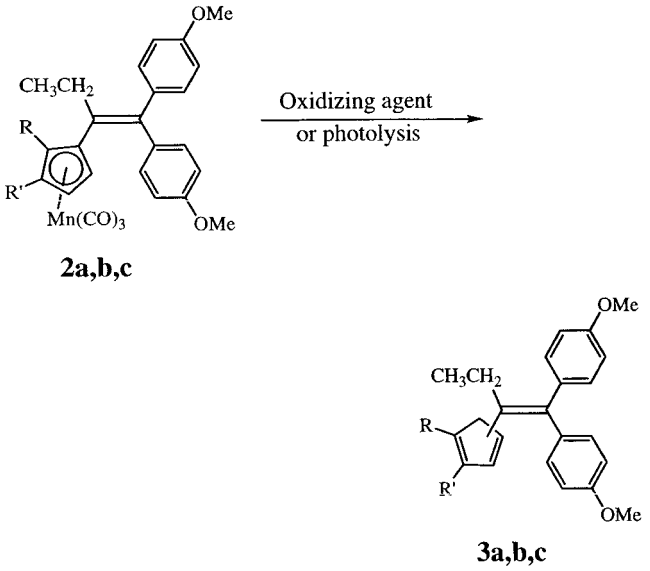
Scheme 2



Scheme 3



Ceric ammonium nitrate[34] and iodine[35] have each been used to oxidize (arene)$Cr(CO)_3$ complexes so as to release the free arene; likewise, ferric nitrate brings about the efficient decomplexation of (alkyne)$Co_2(CO)_6$ clusters.[36] Addition of $(NH_4)_2[Ce(NO_3)_6]$ to a solution of **2a** in THF, or in a THF/methanol mixture, caused considerable evolution of gas and complete disappearance of the cymantrene complex. Thin-layer chromatography yielded an orange material, more polar than **2a**, whose NMR spectrum indicated the formation of a complex mixture of organic products, none of which were the desired cyclopentadiene **3a**, shown in Scheme 3. Likewise, treatment of **2a** with ferric nitrate also resulted in the destruction of the starting material without detectable formation of **3a**. In contrast, when a THF solution of **2a** and iodine was heated for 1 h at 60 °C, 98% of the manganese complex was recovered unchanged.

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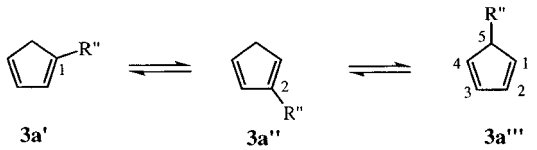
Scheme 4



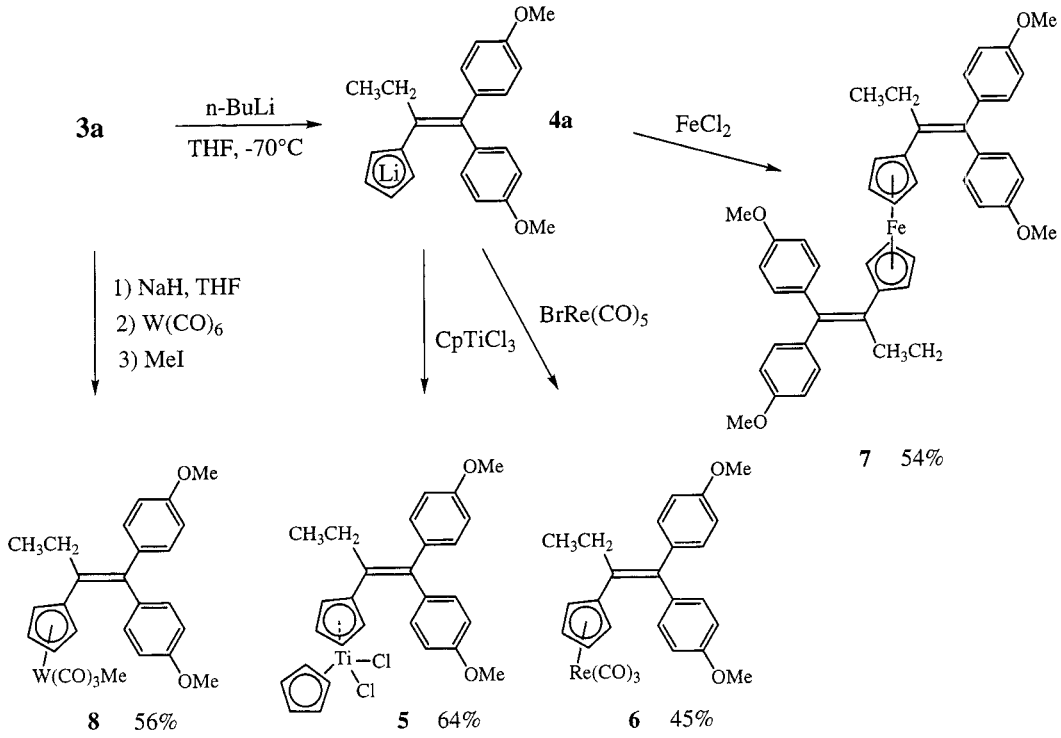
Photolytic Decomplexation Methods. By analogy to our earlier use of sunlight to bring about the decomplexation of (arene)$Cr(CO)_3$ complexes, exposure of an ethereal solution of **2a** to daylight for 1 h led to the complete disappearance of the starting material but yielded, after chromatographic separation, only 14% of the required cyclopentadiene **3a**. Moreover, numerous other orange products were observed whose NMR spectra in the vinyl region bore a close resemblance to that of the material resulting from the attempted decomplexations using Ce(IV) or Fe(III) salts. When a solution of **2a** in 50/50 ether/methanol was exposed to sunlight, the yield of **3a** improved to 34%.

Encouraged by these observations, decomplexations were then attempted with use of a high-pressure mercury lamp that covered the range from 240 nm into the visible region, with a dominant line at 366 nm; a Pyrex filter was used to remove wavelengths below 300 nm. Under these conditions, irradiation of an anhydrous ether solution of **2a** for 45 min yielded 19% of **3a** and 21% recovery of starting material; addition of a trace of trifluoracetic acid to the previous solution boosted the yield of **3a** after photolysis to 50%. More impressively, when the solvent was changed to 2:1 methanol/ether, the isolated yield of **3a** after chromatographic purification was 80%. Application of these latter conditions to the methyl derivatives **2b**,**c** produced the corresponding cyclopentadienes **3b**,**c** in excellent yields, 82% and 91%, respectively. The cyclopentadienes are relatively stable against polymerization and can be kept for several days with refrigeration.

It is evident that monosubstitution of a cyclopentadiene can lead to the three isomers shown in Scheme 4. However, the NMR spectra of **3a** reveal the presence of only two isomers, each of which possesses a methylene group, thus eliminating the 5-substituted isomer **3a‴** as a possibility. Careful scrutiny of the $^1H-^1H$ COSY and $^1H-^{13}C$ shift-correlated 2D spectra allowed the 1- and 2-substituted isomers **3a′** and **3a″**, respectively, to be distinguished. When initially produced, isomer **3a″** is favored over **3a′** by a ratio of approximately 2:1 but, after a period of 9 days in the NMR tube, the spectra of the sample were reacquired and revealed that this isomeric ratio had been essentially reversed. Apparently, the linearly fully conjugated system **3a′** is the thermodynamically favored product. However, since these cyclopentadienes are deprotonated as the first step in their use as reagents for the preparation of cyclopentadienyl derivatives of other metals, separation is not necessary.

To identify the hydrogen source necessary for the generation of the cyclopentadiene **3a**, the photolyses were repeated in the presence of a small quantity of D_2O (0.4 mL in 20 mL of ether). Irradiation for 20 min gave a 32% yield of **3a**; incorporation of the deuterium label into the cyclopentadiene ring was established not only from the diminution of the intensity of the methylene

Scheme 5



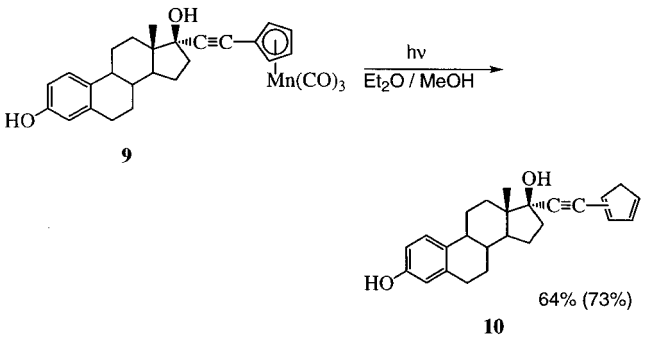
resonances in the NMR spectrum but also from the mass spectrum that clearly exhibited a parent peak for the monodeuterated cyclopentadienes. Similar results were observed with CD_3OD.

Syntheses of Ti, Fe, W, and Re Complexes. The ready availability of the functionalized cyclopentadiene **3a** permits the incorporation of a variety of other organometallic fragments. Typically, as exemplified in Scheme 5, treatment of **3a** with butyllithium, to give **4a**, followed by addition of $CpTiCl_3$, $BrRe(CO)_5$, or $FeCl_2$ yields the corresponding cyclopentadienyl complexes **5**−**7**, respectively, in yields ranging from 45 to 64%. The tungsten complex **8** was prepared by deprotonation using sodium hydride, reaction with $W(CO)_6$, and finally addition of methyl iodide. The rhenium complex **6** is also preparable from the thallium salt of **3a**. Although no attempts have been made to optimize the yields of **5**−**8**, the viability of the method has been clearly established.

Decomplexation of a Mn Complex of Ethynylestradiol. Gratifyingly, photolysis of cymantrene complexes in protic media is also applicable to the hormonal system **9** and produces the free ligand **10** in 64% yield (73% based on starting material consumed; Scheme 6). We are unaware of any previous syntheses of uncomplexed hormonal cyclopentadienes, but we note the very recent report by Cesati and Katzenellenbogen that rhenium complexes of such molecules are, in principle, preparable via their stannylation methodology.[37]

Other potential routes to **10** and related systems could, for example, involve either a palladium coupling procedure to incorporate an alkynyl substituent[38] or treatment of an appropriate cyclopentenone with an acetylide.[39] Nevertheless, the present approach provides a convenient, inexpensive, and relatively high yield route to a series of bio-organometallic molecules of intense current interest.

Scheme 6



Infrared Study. $CpMn(CO)_2(L)$ complexes are known for many types of ligands L.[40] In general, they are obtained by photolysis of $CpMn(CO)_3$ in the presence of the ligand and give rise to two ν_{CO} stretches in the infrared. The compound $(C_5H_5)Mn(CO)_2(THF)$ exhibits IR bands at 1921 and 1850 cm^{-1} but decomposes gradually over the course of time.[40a] When the manganese tricarbonyl complex **2a** was photolyzed in THF, and the progress of the reaction was monitored by IR, the corresponding $Cp'Mn(CO)_2(THF)$ was found to absorb at 1850 cm^{-1}, but the second band anticipated at ~1920 cm^{-1} is obscured by unreacted starting material. After irradiation for 45 min, when approximately 50% of **2a** had reacted, the photolysis was stopped. The reaction mixture was left at ambient temperature overnight,

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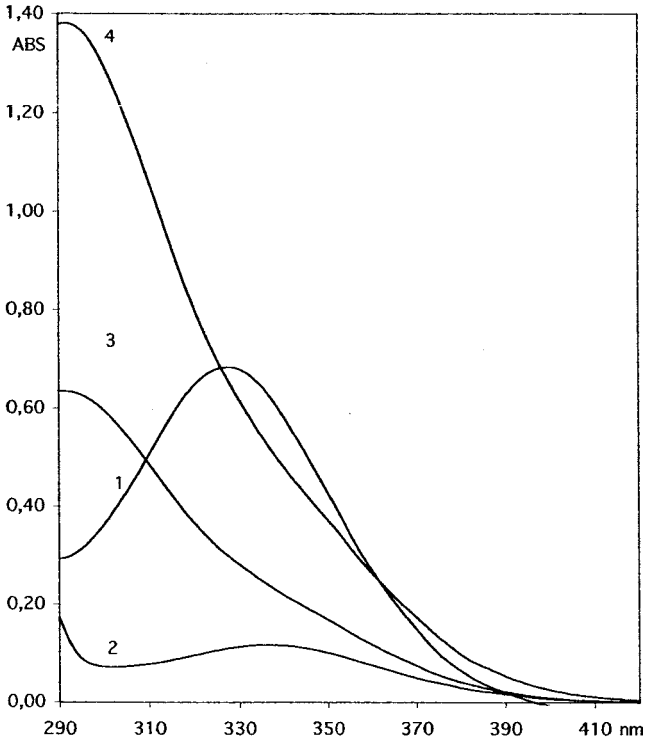


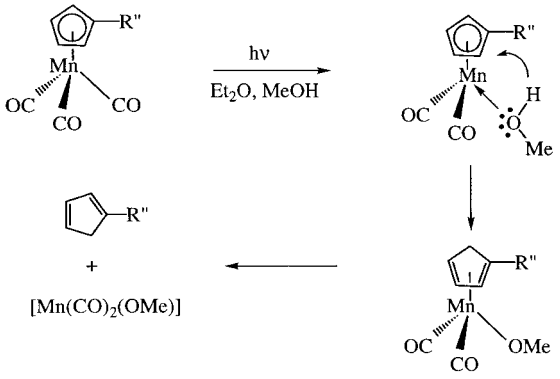
Figure 1. UV−visible spectra: (1) $(C_5H_5)Mn(CO)_3$ (6.25×10^{-4} M); (2) steroidal cymantrene complex **9** (10^{-4} M); (3) cymantrene complex **2a** (10^{-4} M); (4) methylcymantrene complex **2c** (10^{-4} M).

after which time all the $Cp'Mn(CO)_2(THF)$ had decomposed, but no cyclopentadiene **3a** had formed. In contrast, a parallel experiment, in which **2a** was photolyzed in 50/50 ether/methanol for 50 min, yielded an IR spectrum showing intense absorptions at 1921 and 1850 cm^{-1}, implying the formation of $Cp'Mn(CO)_2(MeOH)$. After 2 h irradiation, all ν_{CO} bands had disappeared, and subsequent chromatography furnished **3a** in 38% isolated yield. The relatively low yield is attributable to successive removal of samples for IR analysis.

Mechanistic Implications. The generation of a cyclopentadiene derived by decomposition of a cymantrene requires a source of a proton, or a hydrogen atom, presumably from the solvent. Indeed, the use of deuterated solvents, such as D_2O or CD_3OD, as described above, supports this view. These studies have also shown that classic oxidants, such as ceric or ferric salts, do not lead to formation of the free cyclopentadiene. In contrast, UV photolysis in a protic solvent (methanol, water, or trifluoroacetic acid) provides a perfectly acceptable route to the required dienes.

It is evident that these two approaches do not follow the same pathway; one can reasonably assume that classic chemical oxidants generate cyclopentadienyl radicals or radical cations. However, even in methanol, which can function as either a proton donor or a source of hydrogen radicals, the desired cyclopentadiene is not formed; instead, the products appear to be a complex mixture, perhaps derived from radical coupling reactions. It is well-known that cymantrenes undergo photolysis; as illustrated in Figure 1, the parent molecule $(C_5H_5)Mn(CO)_3$ exhibits an absorption maximum at 330 nm.[40a] Figure 1 also shows data for the cymantrenes **2a,c**, as well as for the (ethynylestradiol)manganese complex **9**. The former possesses only a rather weak absorption around 350 nm but nevertheless does absorb light as far as 420 nm. In contrast, the hormonal derivative has an absorption maximum at 336 nm, with a molar extinction coefficient of 1100.

Scheme 7



When **2a** is irradiated, even with sunlight, formation of the free cyclopentadiene **3a** is observed, the yield depending on the particular experimental conditions. The initially formed 16-electron species $Cp'Mn(CO)_2$ can be stabilized, either strongly by good Lewis bases such as phosphines or weakly by such ligands as THF. However, in the latter case, decomposition does not lead to diene formation, unless the coordinating ligand is also a proton donor. The IR data presented already implicate $Cp'Mn(CO)_2(MeOH)$ as a viable intermediate, and it is reasonable to postulate that intramolecular proton transfer to the five-membered ring generates the corresponding (η^4-cyclopentadiene)$Mn(CO)_2OMe$ complex, which decomposes with liberation of the diene, as depicted in Scheme 7.

Alternatively, one could envisage an oxidative addition process to give $(Cp')Mn(CO)_2(H)(OMe)$, by analogy to the formation of $(C_5H_5)Mn(CO)_2(H)(SiEt_3)$ when cymantrene is irradiated in the presence of $HSiEt_3$.[41] However, in view of the well-established proclivity of cymantrene derivatives, especially complexes of the type $Cp'Mn(CO)[PR_3]_2$, to undergo protonation at the relatively basic metal center,[42] an oxidative addition process is considered an unlikely eventuality in the present case.

Conclusions

This work has shown that it is possible to generate cyclopentadienes by a simple photolytic decomplexation of the corresponding cymantrene. It has been clearly demonstrated that a proton source, such as an alcohol, water, or a carboxylic acid, is necessary to obtain the cyclopentadiene in synthetically useful yields. The mechanism proposed involves photolytic elimination of a carbonyl group, coordination of the ROH ligand, intramolecular proton (or deuteron) transfer to form the η^4-cyclopentadiene, and finally, liberation of the desired diene.

This method allows the synthesis of multifunctionalized cyclopentadienes not accessible by present proce-

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dures and has even been applied to a hormonal steroid. Moreover, the ready availability of these cyclopentadienes facilitates the syntheses of a wide range of other metal complexes, as exemplified by the Ti, Fe, Re, and W systems described herein. We believe that this new approach will offer a variety of new perspectives in organometallic chemistry.

Experimental Section

General Data. Starting materials were synthesized using standard Schlenk techniques, under an argon atmosphere; the 17α-ethynylestradiol complex **9** was prepared as previously described.[21] Anhydrous THF and diethyl ether were distilled from sodium/benzophenone. Methanol (Prolabo) was used without any further purification. Thin-layer chromatography was performed on silica gel 60 GF254. UV photolyses were carried out with a Heraeus TQ150 150 W high-pressure Hg lamp. FT-IR spectra were recorded on a BOMEM Michelson-100 spectrometer. ^{1}H and ^{13}C NMR spectra were acquired on Bruker 200, 250, and 400 MHz spectrometers. Mass spectrometry was performed on a Nermag R 10-10C spectrometer. Melting points were measured with a Kofler device. Elemental analyses were performed by the Regional Microanalysis Department of the Université Pierre et Marie Curie.

(Propionylcyclopentadienyl)tricarbonylmanganese (1a). In a Schlenk tube purged with argon, cymantrene (3.00 g, 14.70 mmol) and propionyl chloride (1.35 g, 14.70 mmol) were dissolved in carbon disulfide (30 mL). $AlCl_3$ (0.977 g, 7.35 mmol) was added in small portions to the solution of cymantrene, and the solution became red. After 1.5 h, the CS_2 was removed under vacuum and the oil obtained was hydrolyzed with water at 0 °C. After extraction with diethyl ether (3 × 20 mL) and drying over magnesium sulfate, the solution was concentrated, whereupon addition of pentane yielded (propionylcyclopentadienyl)tricarbonylmanganese (3.540 g, 92%) as a yellow powder. Recrystallization from diethyl ether/pentane furnished yellow crystals, mp 250 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.44 (t, 2H, J = 2.1 Hz, η^5-C_5H_4), 4.85 (t, 2H, J = 2.1 Hz, η^5-C_5H_4), 2.64 (q, 2H, CH_2), 1.17 (t, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 197.9 (CO), 91.5 (C_1 of η^5-C_5H_4), 86.4 (2C, C_5H_4), 83.4 (2C, C_5H_4), 32.2 (CH_2), 7.9 (CH_3). IR (CH_2Cl_2): ν_{CO} at 2030 (s), 1948 (s), 1686 cm^{-1} (m). Anal. Calcd for $C_{11}H_9O_4Mn$: C, 50.79, H, 3.46. Found: C, 50.83, H, 3.41.

(2-Methyl-1-propionylcyclopentadienyl)- and (3-Methyl-1-Propionylcyclopentadienyl)tricarbonylmanganese (1b,c). As for the synthesis of **1a**, (η^5-C_5H_4Me)Mn(CO)$_3$ (4.150 g, 19 mmol), propionyl chloride (2.560 g, 27.6 mmol), and $AlCl_3$ (2.530 g) gave, after workup, a crude product that was chromatographed on a silica gel column with 1:10 ethyl ether/petroleum ether as eluent. The first to elute was **1b** (1.240 g, 23.7%) as a yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.28 (s, 1H), 4.71 (m, 2H) (η^5-C_5H_3), 2.65 (q, 2H, CH_2CH_3), 2.28 (s, 3H, COCH_3), 1.16 (t, 3H, CH_2CH_3). Anal. Calcd for $C_{12}H_{11}O_4Mn$: C, 52.57, H, 4.04. Found: C, 52.47, H, 4.06. Subsequently, **1c** (2.140 g, 41.3%) was collected as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.35 (s, 1H), 5.27 (s, 1H), 4.70 (s, 1H) (η^5-C_5H_3), 2.59 (q, 2H, CH_2CH_3), 2.03 (s, 3H, COCH_3), 1.16 (t, 3H, CH_2CH_3). Anal. Calcd for $C_{12}H_{11}O_4Mn$: C, 52.57, H, 4.04. Found: C, 52.71, H, 4.35.

1,1′-Bis(*p*-anisyl)-2-cymantrenyl-1-butene (2a). $TiCl_4$ (1.71 g, 9 mmol) was added dropwise to a suspension of zinc powder (1.17 g, 12 mmol) in THF (30 mL) at 0 °C. The blue mixture obtained was heated at reflux for 2 h, the solution became black, and the oil bath was removed. A second solution was prepared by dissolving 4,4′-dimethoxybenzophenone (0.882 g, 3 mmol) and propionylcymantrene (**1a**; 0.780 g, 3 mmol) in THF (15 mL). The latter solution was added dropwise to the first solution, and the resulting mixture was then heated again for 2 h. After it was cooled to room temperature, the mixture was hydrolyzed with 100 mL of a 10% Na_2CO_3 solution. After ether extraction and solvent removal, the crude product (2.12 g) was chromatographed on silica gel plates with 1:5 ethyl ether/pentane as eluent to give **2a** (1.25 g, 83% yield). Recrystallization from ethyl ether/pentane furnished yellow crystals, mp 91 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.10 (d, 2H), 7.01 (d, 2H), 6.84 (d, 2H), 6.80 (d, 2H) (aromatic rings), 4.54 (t, 2H), 4.47 (t, 2H) (C_5H_4), 3.81 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 2.31 (q, 2H, CH_2CH_3), 1.05 (t, 3H, CH_2CH_3). Anal. Calcd for $C_{26}H_{23}O_5Mn$: C, 66.38, H, 4.93. Found: C, 66.45, H, 5.00.

1,1′-Bis(*p*-anisyl)-2-(2-methylcymantrenyl)-1-butene (2b). Following the procedure used for **2a**, 4,4′-dimethoxybenzophenone (0.726 g, 3 mmol), zinc (1.170 g, 18 mmol), $TiCl_4$ (1.710 g, 9 mmol), and **1b** (0.822 g, 3 mmol) yielded **2b** (0.937 g, 64%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.10 (d, 2H), 6.89 (d, 2H), 6.85 (d, 2H), 6.65 (d, 2H) (aromatic rings), 4.86 (m, 1H), 4.46 (m, 1H), 4.36 (m, 1H) (C_5H_3), 3.83 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 2.30 (m, 2H, CH_2CH$_3$), 1.40 (s, 3H, Me), 1.12 (t, 3H, J = 7.5 Hz, CH_2CH_3). MS (EI, 70 eV): m/z 484 [M$^+$], 400 [(M − 3CO)$^+$].

1,1′-Bis(*p*-anisyl)-2-(3-methylcymantrenyl)-1-butene (2c). Analogously, 4,4′-dimethoxybenzophenone (2.270 g, 9.35 mmol), zinc (2.860 g, 44 mmol), $TiCl_4$ (6.900 g, 36.39 mmol), and **1c** (2.550 g, 9.30 mmol) yielded **2c** (2.15 g, 48%) as a yellow solid, mp 74 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.09 (d, 2H), 7.02 (d, 2H) (aromatic ring), 6.85 (d, 2H), 6.81 (d, 2H) (aromatic ring), 4.39 (s, 2H), 4.29 (s, 1H) (C_5H_3), 3.80 (s, 6H, OCH_3's), 2.28 (m, 2H, CH_2CH$_3$), 1.83 (s, 3H, Me), 1.03 (t, 3H, J = 7.3 Hz, CH_2CH_3). IR (CH_2Cl_2): ν_{CO} 2012, 1926 cm^{-1}. MS (EI, 70 eV): m/z 484 [M$^+$], 400 [(M − 3CO)$^+$], 55 [Mn$^+$]. Anal. Calcd for $C_{27}H_{25}O_5Mn$: C, 66.94, H, 5.16. Found: C, 66.81, H, 5.30.

Chemical Oxidations of 2a. (a) When $(NH_4)_2Ce(NO_3)_6$ (0.274 g, 0.5 mmol) was added to **2a** (0.056 g, 0.12 mmol) in 1:1 THF/methanol (2 mL), gas evolution was evident and the solution became orange with complete dissolution of the cerium salt. After it was stirred for 2 h, the solution was concentrated and chromatographed on silica gel plates with 1:3 ethyl ether/pentane as eluent. An orange fraction (20 mg) was isolated, and **2a** had completely disappeared. The NMR spectrum of this mixture of organic compounds could not be assigned.

(b) When iodine (0.152 g, 0.6 mmol) was added to **2a** (0.140 g, 0.3 mmol) in THF (15 mL), and the mixture was stirred at room temperature for 3 h and then at 60 °C for 1 h, 98% of starting material was recovered after workup.

(c) When powdered $Fe(NO_3)_3$ (0.500 g, 0.9 mmol) was added to **2a** (0.140 g, 0.3 mmol) in dichloromethane (15 mL), the solution became orange and then brown after 4.5 h of stirring. After separation by TLC, **2a** (0.008 g, 6%) and an orange fraction (0.028 g) were obtained. The NMR spectrum of the orange fraction appeared to be identical with that isolated from the reaction with ceric ion.

Photolysis Reactions. (a) In Sunlight. When **2a** (0.110 g, 0.23 mmol) was dissolved in technical grade diethyl ether (5 mL), and the solution was exposed to sunlight for 1 h, a brown powder precipitated from the solution. The remaining solution was subjected to TLC on silica gel using 1:6 ethyl ether/pentane as eluent to give **3a** (0.011 g, 14%) as a beige oil, together with 0.039 g of an unidentified orange oil. In a parallel experiment, using 1:2 diethyl ether/methanol as the solvent, **3a** (34%) was isolated and **2a** (20.6%) was recovered.

(b) UV Irradiations. (i) When a long tube containing **2a** (0.402 g, 0.85 mmol) dissolved in a mixture of technical grade ethyl ether (15 mL) and methanol (30 mL) was irradiated using a UV lamp (TQ150), significant gas evolution was observed and, after 1 h, a brown powder precipitated. The solution was filtered through a filter funnel filled with silica gel of thickness 0.5 mm, and the solvent was subsequently removed by evaporation. TLC on silica gel with 1:6 ethyl ether/pentane as eluent gave **3a** (0.228 g, 81%) as a beige oil, whose NMR indicated the presence of two isomers. ^{1}H NMR of major

product, **3a″** (200 MHz, $CDCl_3$): δ 7.10 (d, 2H), 6.86 (d, 2H) (aromatic ring), 6.96 (d, 2H), 6.70 (d, 2H) (aromatic ring), 6.25 (pseudoquintet, $J \approx 1.5$ Hz, 1H, H_1), 6.19 (dd, $J \approx 5$ Hz, $J \approx 1.5$ Hz, H_3), 5.95 (doublet of pseudoquartets, $J = 5.1$ Hz, $J = 1.4$ Hz, H_4), 3.83 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.01 (m, 2H, CH_2 of Cp ring), 2.42 (q, 2H, CH_2CH_3), 1.01 (t, CH_2CH_3). A second isomer, **3a′**, about one-third of the mixture, was distinguished from the first by the following NMR signals: δ 6.45 (d,t, $J \approx 5$ Hz, $J \approx 1$ Hz, H_4), 6.41 (m, 1H) 6.20 (m, H_3), 3.81 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 2.65 (m, 2H, CH_2 of Cp ring), 2.41 (q, 2H, CH_2CH_3), 1.02 (t, CH_2CH_3).

(ii) UV photolysis of **2a** in anhydrous diethyl ether alone gave **3a** (19%) and **2a** (21% recovered). Photolysis of **2a** in diethyl ether containing 2 drops of CF_3COOH gave a 50% yield of **3a**.

(iii) When **2a** (0.141 g, 0.3 mmol) was dissolved in anhydrous ethyl ether (15 mL) and CD_3OD (99.8% D) (2 mL), and the solution was irradiated for 30 min, chromatographic separation gave **3a-***d* (0.029 g, 32%), together with recovered starting material **2a** (0.055 g, 39%). MS (EI, 70 eV): *m*/*z* 333 $[M]^+$, 304, 289, 273.

(iv) When **2a** (0.141 g, 0.3 mmol) was dissolved in anhydrous ethyl ether (15 mL) and D_2O (99.9%-D) (0.4 mL) and the solution was irradiated for 40 min, chromatographic separation gave **3a-***d* (0.032 g, 32%) together with recovered starting material **2a** (0.020 g, 14%).

(v) Following the procedure above, **2b** (0.301 g, 0.62 mmol) was irradiated for 40 min. Chromatography on silica gel plates with 1:10 ethyl ether/pentane as eluent gave **3b** (0.176 g, 82%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.15−6.60 (m, 8H) (aromatic rings), 6.50−6.20 (m, 2H, C_5H_3 ring), 3.83 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.04, 2.75 (CH_2's of C_5H_4 ring isomers), 2.27, 2.26 (2 q, 2H, CH_2CH_3), 1.64 (s, 3H, Me), 0.94 (t, 3H, $J = 7.2$ Hz, $-CH_2CH_3$).

(vi) As described above, **2c** (0.144 g, 0.30 mmol) was irradiated for 45 min. Chromatography on silica gel plates with 1:10 ethyl ether/pentane as eluent gave **3c** (0.094 g, 91%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13−6.69 (m, 8 H) (aromatic rings), 2.36 (m, 2H, CH_2CH_3), 1.92 (s, 3H, Me), 1.09 (m, 3H, CH_2CH_3); first isomer, 6.25 (s, 1H), 6.01 (s, 1H), (C_5H_3 ring), 3.83 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 2.88 (s, 2H, CH_2 of C_5H_4 ring); second isomer, 6.01 (s, 1H), 5.56 (s, 1H) (C_5H_3 ring), 3.82 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 2.61 (s, 2H, CH_2 of C_5H_3 ring).

(vii) When **9** (0.100 g, 0.2 mmol) dissolved in technical grade ethyl ether (10 mL) and methanol (10 mL) was irradiated for 30 min, a brown powder precipitated. The solution was filtered through a filter funnel filled with silica gel of thickness 0.5 mm, and the solvent was subsequently removed by evaporation. TLC on silica gel with 2:3 ethyl ether/pentane as eluent gave the decomplexed steroidal cyclopentadiene **10** (0.047 g, 64%) as a colorless oil, together with recovered **9** (0.013 g). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.16 (d, 1H, H_1), 6.77 (m, 1H of Cp ring), 6.65 (dd, 1H, H_2), 6.58 (d, 1H, H_4) 6.51 (m, 1H of Cp ring), 6.40 (m, 1H of Cp ring), 3.15 (m, 2H of Cp ring), 2.81 (m, 2H, H_6) 0.93 (s, 3H, Me_{13}).

Infrared Measurements. In a Schlenk tube, **2a** (0.110 g, 0.23 mmol) was dissolved in anhydrous THF (10 mL) and subjected to UV irradiation. Every 20 min, a small sample of the solution was syringed into an argon-purged infrared cell and the spectrum quickly recorded. Two bands at 1921 and 1850 cm^{-1} grew in while the IR bands of the starting complex progressively decreased. After 55 min of irradiation, the solution was left in the tube overnight, but the intermediate Cp′Mn$(CO)_2$(THF) had completely decomposed without forming **3a**. In an identical experiment using 1:1 diethyl ether/methanol as a solvent, two bands appeared at 1921 and 1850 cm^{-1}; subsequently, **3a** was isolated in 38% yield.

Synthesis of Titanium Complex 5. Freshly prepared **3a** (0.262 g, 0.79 mmol) dissolved in THF (4 mL) was cooled to −70 °C, and *n*-BuLi (0.87 mL of a 1.6 M solution in hexane, 0.95 mmol) was added dropwise. The solution of the lithium salt **4a** was stirred for 1.5 h while the temperature was allowed to rise slowly to −20 °C, and the solution became orange. The solution was recooled to −70 °C, then $CpTiCl_3$ (0.262 g, 1.19 mmol) was added as a solid in one portion, and the solution immediately turned dark red. After the mixture was stirred for 3 h, the THF was removed under vacuum and the residue was dissolved in dichloromethane; after filtration and removal of solvent, **5** (0.260 g, 64%) was obtained as a red solid and was recrystallized from CH_2Cl_2/pentane to give red-black crystals, mp 216 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.20 (d, 2H), 6.88 (d, 2H) (aromatic ring), 7.00 (d, 2H), 6.81 (d, 2H) (aromatic ring), 6.49 (s, 5H, C_5H_5), 6.27 (t, 2H), 6.15 (t, 2H) (C_5H_4), 3.82 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 2.44 (q, 2H, CH_2CH_3), 1.00 (t, 3H, CH_2CH_3). MS (DCI): *m*/*z* 532 $[(M + NH_4)^+]$, 333. Anal. Calcd for $C_{28}H_{28}Cl_2O_2Ti$: C, 65.26, H, 5.48. Found: C, 65.41, H, 5.52.

Synthesis of Rhenium Complex 6. (a) From a Lithium Salt. The lithium salt **4a** was prepared from **3a** (0.075 g, 0.22 mmol) as described above, and a solution of $BrRe(CO)_5$ (0.089 g, 0.22 mmol) in THF (2 mL) was added at 0 °C. The mixture was heated at reflux for 2.5 h, and after hydrolysis with ice water, ether extraction, and solvent removal, the residue was chromatographed on silica gel plates using 1:9 ether/pentane as eluent to give **6** (0.060 g, 45% yield), mp 110 °C, as a colorless solid. IR (CH_2Cl_2): ν_{CO} at 2017 (s) and 1923 cm^{-1} (s). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.08 (d, 2H), 6.85 (d, 2H) (aromatic ring), 7.03 (d, 2H), 6.80 (d, 2H) (aromatic ring), 5.11 (t, 2H), 5.07 (t, 2H) (C_5H_4), 3.80 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 2.27 (q, 2H, CH_2CH_3), 1.07 (t, 3H, CH_2CH_3). MS (EI, 70 eV): *m*/*z* 602 $[M^+]$, 518 $[(M - 3CO)^+]$, 220, 205. Anal. Calcd for $C_{26}H_{23}O_5Re$: C, 51.90, H, 3.85. Found, C, 51.82, H, 3.83.

(b) From a Thallium Salt. Freshly prepared **3a** (0.075 g, 0.22 mmol) dissolved in diethyl ether (1 mL) was cooled to 0 °C and treated with TlOEt (0.110 g, 0.44 mmol), and the solution was stirred for 15 min at 0 °C before the cooling bath was removed and the stirring maintained for another 15 min. After removal of the solvent, the yellow solid obtained was washed with pentane (3 mL) and $BrRe(CO)_5$ (0.089 g, 0.22 mmol) in THF (4 mL) was added. The mixture was heated at reflux for 4 h, and a white solid precipitated from the solution. After filtration and removal of most of the solvent, the crude product was chromatographed on silica gel plates using 1:9 ether/pentane as eluent to give **6** (0.049 g, 37% yield).

Synthesis of Iron Complex 7. As described above, the lithium salt **4a** was prepared from **3a** (0.361 g, 1.08 mmol), recooled to −50 °C, and treated with $FeCl_2$ (0.068 g, 0.54 mmol) in THF (10 mL), and the mixture was heated at reflux for 1 h. After hydrolysis with ice water, ether extraction (3 × 30 mL), and solvent removal, the residue was chromatographed on a silica gel column using 1:1 ethyl ether/pentane as eluent to give **7** (0.390 g, 54%) as a red solid, mp 196 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.07 (d, 2H), 6.85 (d, 2H) (aromatic ring), 6.94 (d, 2H), 6.76 (d, 2H) (aromatic ring), 4.05 (m, 2H), 3.80 (m, 2H) (C_5H_4), 3.81 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 2.59 (q, 2H, CH_2CH_3), 1.02 (t, 3H, CH_2CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 157.8, 137.5, 137.1, 136.5, 131.1, 130.5, 113.4, 113.3 (C_6H_4's; C═C), 87.8, 70. 6, 69.1 (C_5H_4), 55.1 (OMe), 27.9 (CH_2-CH_3), 15.4 (CH_2CH_3). MS (EI, 70 eV): *m*/*z* 718 $[M^+]$, 387, 330, 149. Anal. Calcd for $C_{46}H_{46}O_4Fe$: C, 76.88, H, 6.45. Found, C, 76.79, H, 6.43.

Synthesis of Tungsten Complex 8. NaH (0.059 g, 1.3 mmol) (dispersion in mineral oil) was placed in a Schlenk tube and washed with hexane, and THF (12 mL) was added. After the mixture was cooled to 0 °C, a solution of **3a** (0.031 g, 0.93 mmol) in THF (2 mL) was added dropwise; the solution became purple after stirring for 1 h, and $W(CO)_6$ (0.515 g, 1.47 mmol) was added in one portion. The mixture was heated at reflux overnight, the solution was cooled again to −20 °C, MeI (1.240 g, 8.73 mmol) was added, and the stirring was maintained for 5 h. After hydrolysis with ice water, ether extraction, and

solvent removal, the residue was chromatographed on silica gel plates using 1:4 ether/pentane as eluent to give **8** (0.319 g, 56%) as a colorless solid, mp 93 °C. IR (cyclohexane): ν_{CO} at 2014 (s) and 1925 cm^{-1} (s). ^1H NMR (200 MHz, $CDCl_3$): δ 7.11 (d, 2H), 6.87 (d, 2H) (aromatic ring), 7.03 (d, 2H), 6.81 (d, 2H) (aromatic ring), 5.14 (t, 2H), 4.96 (t, 2H) (C_5H_4), 3.81(s, 3H, OC*H*$_3$), 3.80 (s, 3H, OC*H*$_3$), 2.32 (q, 2H, *C*H_2CH$_3$), 1.05 (t, 3H, CH$_2$*C*H_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 236.3 (CO's), 158.5, 158.3, 136.1, 135.7, 130.4, 130.1, 114.1, 113.7 (C_6H_4), 142.7, 130.7 (C═C), 91.5, 89.3 (C_5H_4), 55.1 (OMe), 28.0 (*C*H_2CH$_3$), 15.0 (CH$_2$*C*H_3), 9.7 (W−Me). MS (EI, 70 eV): *m*/*z* 614 [M^+], 529, 515 [$(M - 3CO - Me)^+$], 484. Anal. Calcd for $C_{27}H_{26}O_5W$: C, 52.78, H, 4.27. Found, C, 52.87, H, 4.28.

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