Palladium-Catalyzed Chloride Substitution of η^5-(Chlorocyclohexadienyl)$Mn(CO)_3$ Complexes: An Access to Novel η^6-(Arene)$Mn(CO)_3^+$ Cations

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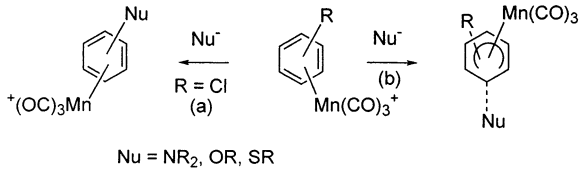
Functionalization of η^5-(chlorocyclohexadienyl)$Mn(CO)_3$ complexes was achieved by palladium-catalyzed reactions using $Pd_2(dba)_3$ in the presence of $AsPh_3$. Arylation, carbonylation, and substitution by alkyne-, alkene-, and heteroatom-based nucleophiles were performed, giving rise to functionalized η^5 complexes whose structures have been investigated by NMR and X-ray studies. These η^5 complexes are valuable precursors upon *exo*-hydride abstraction, of the corresponding η^6 cations, substituted by resonance-withdrawing groups, whose conformations in solution and in the solid state have been studied.

Introduction

Arene activation by a tricarbonylmetal fragment greatly modifies the reactivity of the arene ring by imparting high electrophilicity.[1] Among all transition metals commonly used, manganese appears very attractive because of the high electrophilic feature of its corresponding cationic complexes. Nucleophilic attacks on the arene ligand, metal center, or carbonyl ligands have been widely studied.[2] This specific reactivity has been exploited for synthetic purposes and applied to the preparation of natural products.[3] Nevertheless, until now these complexes remained relatively undeveloped compared to their chromium[1e] and iron counterparts.[1f] Indeed, chemistry at the carbon π-system without loss of the metal is mentioned in a mere handful of papers. *Ipso* chloride substitution in η^6-(chloroarene)tricarbonylmanganese complexes allows a clean nucleophile introduction,[4] but it has been demonstrated that such a strategy was restricted to amino, oxo, and thio nucleophiles (eq 1, path a).



(1)

The main reactions that are described for Mn complexes are addition reactions leading to neutral and stable η^5-(cyclohexadienyl)tricarbonylmanganese complexes (eq 1, path b). Only a few studies[5a] dealing with the reactivity of these neutral complexes have been undertaken and involve attack at the terminus of the

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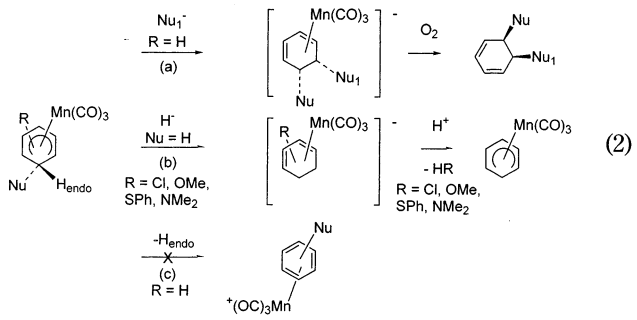
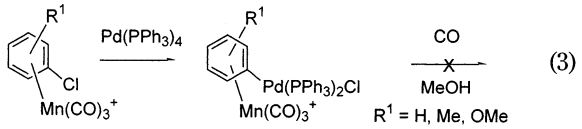
π-system leading to the formation of cyclohexadienes, either via transient anionic η^4-cyclohexadiene Mn complexes,[5c,6] via neutral η^4-dicarbonylnitrosylmanganese complexes,[5d−h] or via an acylmetalate anionic η^5 complex.[5b] The corresponding substituted cyclohexadienes were formed after an oxidative process (eq 2, path a). Several years ago, in the course of the reactivity study of manganese complexes, we described the first *cine* and *tele* nucleophilic substitutions of η^5-(X-substituted-cyclohexadienyl)MnCO$_3$ complexes after treatment with hydrides and a proton source (eq 2, path b).[7] However, the electrophilic character of the cyclohexadienyl ligand is restricted to hydride and stabilized nucleophiles. Another special feature of η^5-(cyclohexadienyl)Mn(CO)$_3$ complexes is their rearomatization, which can only proceed through *exo*-hydride abstraction. In this regard, rearomatization of such complexes obtained through nucleophilic addition into the parent η^6 pattern remains unsuccessful without loss of the metal (eq 2, path c).



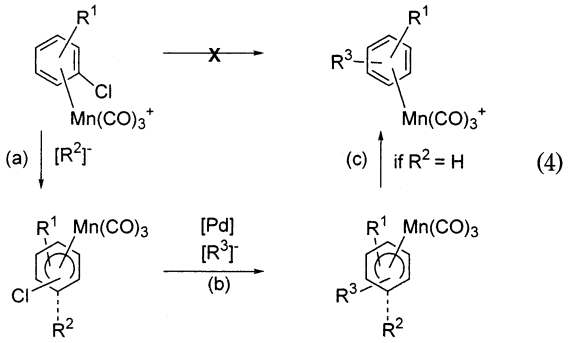
(2)

Whereas the presence of the highly withdrawing Mn$^+$(CO)$_3$ entity renders the carbon−chlorine bond of η^6-(chloroarene) or η^5-(cyclohexadienyl)Mn(CO)$_3$ complexes reactive toward Pd(0) oxidative addition, to our knowledge, no report of palladium-catalyzed functionalization of such complexes has been reported. In contrast to chromium analogues,[9] although the palladium entity inserts into the carbon−chlorine bond of η^6-(chloroarene)-Mn$^+$(CO)$_3$ complexes, the resulting stable bimetallic Mn−Pd complex did not afford any classical coupling product[8] (eq 3).



(3)

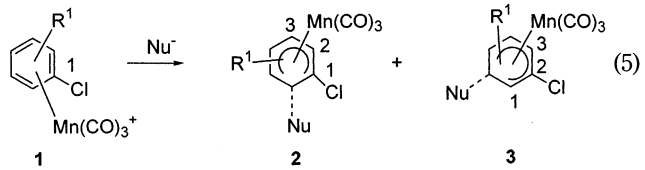
Taking into account the specificity of arene manganese complex chemistry and with the aim of solving the long-standing reactivity problems of such complexes toward Pd-catalyzed reactions, we wish hereby to report a general concept for the functionalization of η^5-Mn(CO)$_3$ complexes based on palladium catalysis (eq 4). We planned to use such reactions in a three-step methodology to synthesize new cationic η^6-(arene)Mn(CO)$_3^+$-complexes starting from η^6-(chloroarene)Mn(CO)$_3^+$. The complete sequence started with hydride addition, leading to neutral η^5 complexes (eq 4, path a). The second step involved a palladium-catalyzed functionalization of the newly formed η^5 derivatives (eq 4, path b). Delivery of the desired η^6-(arene)Mn(CO)$_3^+$ complexes was finally attempted by hydride abstraction (eq 4, path c). In this paper we describe the details of this study along with the structures of novel η^5 and η^6 Mn complexes.



(4)

Results and Discussion

Functionalization of η^5-(Chlorocyclohexadienyl) Mn(CO)$_3$ Complexes. η^5-(Chlorocyclohexadienyl)Mn-(CO)$_3$ complexes, used as starting material in this work, were readily prepared by nucleophilic addition of hydride[4a,6a,10] or phenylmagnesium bromide[11] to various substituted η^6-(chloroarene)Mn(CO)$_3^+$ (eq 5). As already described,[10] hydride addition to chlorobenzene and 4- and 2-chlorotoluene tricarbonylmanganese complexes **1a**, **1b**, and **1d**, respectively, lead to mixtures of two regioisomers. The **2**:**3** ratio strongly depends on electronic effects of the substituents. In contrast, due to the donor ability of the methoxy group in complexes **1c** and **1e**, addition is exclusively directed *ortho* to the chlorine atom, selectively generating complexes **2c** and **2e**.



(5)

1

1a R^1 =4-H
1b R^1 = 4-Me
1c R^1 = 4-OMe
1d R^1 = 2-Me
1e R^1 = 2-OMe

2 (Nu = H)

2a R^1 =4-H
2b R^1 = 4-Me
2c R^1 = 4-OMe
2d R^1 = 2-Me
2e R^1 = 2-OMe

2f R^1 = 4-OMe (Nu = Ph)

3 (Nu = H)

3a R^1 = 5-H
3b R^1 = 5-Me
3d R^1 = 1-Me
3d R^1 = 1-Me

Choice of the Catalytic System. Our study began with the determination of the best catalytic system for the carbon−carbon bond formation. The efficiency of various catalytic systems was compared for the coupling

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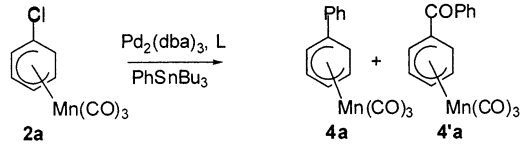
Table 1. Variation of the Nature of L for Stille Reaction



2a **4a** **4'a**

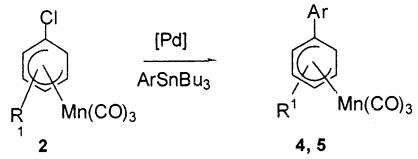
entry	L	reaction time (h)	**4a** (yield %)
1	PPh_3	17.5	
2	dppf	2	
3	$P(OEt)_3$	6	
4	$P(^tBu)_3$	24	
5	$AsPh_3$	20	52
6	$SbPh_3$	4.5	60[a]

[a] Formation of 20% of **4′a** was additionally observed.

reaction between complex **2a** and tributylphenyltin in DMF at room temperature. Pd_2dba_3 was used as precatalyst in combination with different ligands labeled L (Table 1). A Stille type reaction was chosen as a test reaction due to its well-documented mechanism and wide usage. Moreover mild reaction conditions for this process with arene$Cr(CO)_3$ were developed in our laboratory.[9b]

The results obtained with complex **2a** are gathered in Table 1. To our surprise, only decomplexation of the starting material was observed using the classical triphenylphosphine ligand (Table 1, entry 1). The use of an electron-rich bidentate phosphine, dppf, a bulky phosphine, $P(^tBu)_3$, and a phosphite ligand, $P(OEt)_3$, was also unsuccessful (entries 2−4). We next turned our attention to an arsine ligand, $AsPh_3$, and were able to obtain the desired coupling product in 52% yield (entry 5).[9c] Better results with $AsPh_3$ are in agreement with the observations of Farina and co-workers.[12] The acceleration of the transmetalation step in the presence of $AsPh_3$ was correlated to its higher decoordination ability. Nevertheless, the strict selectivity observed cannot be explained. However, we can put forward the hypothesis of an interaction between Mn-, Pd-, and P-based ligands which could be responsible for the hindered formation of the catalytic system, its degradation, and, consequently, its lack of efficiency. As support for our explanation, it has been observed that η^6 complexes were stable in the presence of phosphines,[8] whereas complexes of lower hapticity could be decoordinated under such conditions.[5] To increase the yield of the coupling product, we tried triphenylantimony, $SbPh_3$. In this case two coupling products were isolated: complexes **4a** and **4′a** in 60 and 20% yield, respectively (Table 1, entry 6). In contrast to Farina's results[12a] we obtained high yields of the expected coupling products in a shorter reaction time; however the reaction was less chemoselective. Decomplexation of the starting material, probably favored by the steric hindrance due to the Sb ligand, provided carbon monoxide, involved in the formation of complex **4′**. Formation of carbonylation products under non-carbonylative conditions has already been reported in the case of tricarbonylchromium complexes.[9b,13] The reaction conducted without a catalytic system did not give any new product; there was

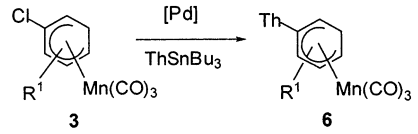
Table 2. Stille Reaction with η^5-(1-Chlorocyclohexadienyl)$Mn(CO)_3$ Complex



2 **4, 5**

entry	R^1	complex	Ar	reaction time (h)	complex (yield %)
1	H	**2a**	Th	18	**5a** (51)
2	4-Me	**2b**	Ph	24	**4b** (45)
3	4-Me	**2b**	Th	20	**5b** (48)
4	4-OMe	**2c**	Th	20	**5c** (78)
5	2-Me	**2d**	Th	20	**5d** (53)

Table 3. Stille Reaction with η^5-(2-Chlorocyclohexadienyl)$Mn(CO)_3$ Complexes



3 **6**

complex **3**	R^1	complex **6** (yield %)
3a	H	**6a** (58)
3b	5-Me	**6b** (30)
3d	1-Me	**6d** (43)

no direct substitution of the chlorine atom. To avoid the problem of separation of two coupling products, we used for the palladium-catalyzed reactions presented in this paper the association of $Pd_2(dba)_3$ and $AsPh_3$ (noted [Pd] in the equations and in the tables), which appeared more efficient and selective.

Stille Reaction. Having in hand a suitable catalytic system, we first examined Stille arylation of several η^5-(1-chloro-R^1-cyclohexadienyl)$Mn(CO)_3$ (**2**, R^1 = 4-Me, 4-OMe, 2-Me) (Table 2).

Thienyltributyltin reacted in the same way as phenyltributyltin (Table 1, entry 5) with complex **2a** to deliver complex **5a** in 51% yield (Table 2, entry 1) as well as with complex **2b** to deliver complexes **4b** and **5b** in 45 and 48% yields, respectively (Table 2, entries 2 and 3). The reaction path is weakly sensitive to the nature and to the position of the R^1 substituent in the π-system (Table 2, entries 3−5). Indeed *ortho*-substituted complex **2d** led to complex **5d** in 53% yield (entry 5). Furthermore, the electron-withdrawing ability of the $Mn(CO)_3$ entity allowed the oxidative addition of $Pd^{(0)}$ even in the presence of an electron-donating substituent (Table 2, entry 4).

Arylation of η^5-(2-chlorocyclohexadienyl)$Mn(CO)_3$ regioisomer **3** with 2-tributylstannylthiophene (noted Th-$SnBu_3$) was also performed under the same reaction conditions (reaction time: 24 h) (Table 3).

Complex **3a** gave the corresponding coupling adduct in a slightly better yield (58%) than the methyl-substituted complexes **3b** and **3d** (30 and 43%, respectively). In these cases, again no strong steric hindrance and substituent effects on the reaction path were observed. However, the yields reported in Table 3 are generally lower than those in Table 2 and reaction times longer (24 h in Table 3). These observations led us to

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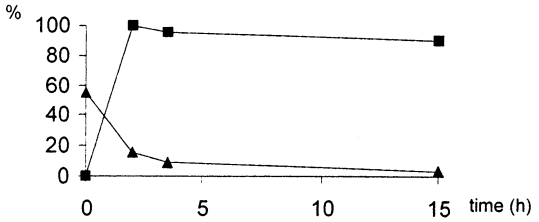
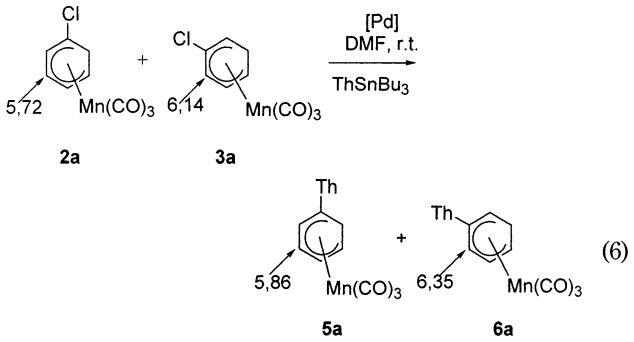


Figure 1. Evolution of percentages of **2a** (▲) and **5a** (■).

postulate that the kinetics of the arylation process could be very different for the 1- and 2-chlorocyclohexadienyl regioisomers. If this hypothesis was confirmed, it would be possible to realize a selective functionalization of one regioisomer starting from a mixture of regioisomers that would avoid purification of the starting η^5 complex. For this purpose, we thought that such an experiment could be monitored by ^{1}H NMR, where integration of H^3 protons could allow the determination of **2a**:**3a** and **5a**:**6a** ratios (eq 6). Indeed ^{1}H NMR spectra showed large differences for the H^3 resonance of complexes **2a** and **3a**: $\delta(H_3)_{\mathbf{2a}}$ = 5.72 ppm and $\delta(H_3)_{\mathbf{3a}}$ = 6.14 ppm. Corresponding coupling products **5a** and **6a** exhibit similar behavior: $\delta(H_3)_{\mathbf{5a}}$ = 5.86 ppm and $\delta(H_3)_{\mathbf{6a}}$ = 6.35 ppm (eq 6). A mixture of complexes **2a** and **3a** in 54:46 ratio was reacted with tributylstannylthiophene under the previously described conditions.



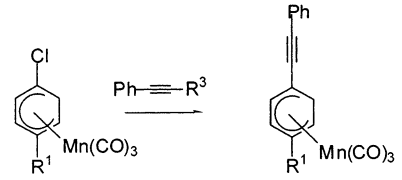
(6)

ThSnBu$_3$ and η^5-(1-chlorocyclohexadienyl)Mn(CO)$_3$ **2a**, which we thought to be the most reactive isomer, were introduced in stoichiometric amount. Evolution of the reaction mixture was followed by ^{1}H NMR (Figure 1). After 2 h, only **2a** reacted, ratios **2a**:**3a** and **5a**:**6a** being 16:84 and 100:0, respectively. The same trend was observed after 3.5 h; that is, the formation of **5a** went on while **3a** hardly began to react. After 15 h the reaction was finished: complex **2a** was almost totally arylated, whereas complex **3a** scarcely reacted.

Surprisingly these data clearly show selective arylation of one regioisomer. Indeed η^5-(1-chlorocyclohexadienyl)Mn(CO)$_3$ reacted faster than η^5-(2-chlorocyclohexadienyl)Mn(CO)$_3$, whereas the arene ring C$_1$ carbon has more sp^3 character than the C$_2$ carbon. Thus electronic effects are in favor of the reverse order of reactivity. However, another explanation for the experimental observations may be steric, as C$_2$ in contrast to C$_1$ is eclipsed by a Mn−CO vector. So the higher steric hindrance of C$_2$ compared to C$_1$ might cause this impressive difference of reactivity.

Introduction of Multiple Bonds. We next investigated the substitution of the chlorine atom of the cyclohexadienyltricarbonylmanganese moiety by a double or a triple C−C bond. We were first interested in the synthesis of alkyne-substituted η^5-cyclohexadienyl complexes, precursors of the corresponding alkyne-substituted η^6-arene complexes that are difficult to obtain by direct complexation.[14] But in a first step, we wanted to verify if direct substitution of the chlorine atom was possible. When reaction was attempted with complex **2a** in the presence of lithium phenylacetylide, no substitution product was isolated and the starting material remained unchanged. Thus, we alternatively tried a Pd-catalyzed reaction. To compare the efficiency of various alkyne coupling methodologies, we performed Sonogashira, Negishi, and Stille reactions to introduce a phenylacetylene moiety to η^5-(chlorocyclohexadienyl)-Mn(CO)$_3$ complex (Table 4). Complex **9** was obtained in 79% yield after 1 h using directly phenylacetylene. Following the Negishi strategy, complex **2c** reacted with in situ generated ethynylbenzene zinc chloride, in the presence of Pd$_2$dba$_3$ and AsPh$_3$ at room temperature in THF to afford after 1 h complex **9** in 77% yield. Finally we investigated the Stille coupling reaction between tributylstannylethynylbenzene and complex **2a** with the same catalytic system in DMF at room temperature. The corresponding alkyne **8** was obtained in 91% yield after 0.5 h. This last procedure represented the most efficient strategy in comparison with the other results gathered in Table 4.

Table 4. Synthesis of Alkyne-Substituted η^5-(Cyclohexadienyl)Mn(CO)$_3$ Complexes



2 **8** R^1 = H, **9** R^1 = OMe

R^1 (complex)	R^3	reaction time (h)	yield (complex)
4-OMe (**2c**)	H	1	79 (**9**)
4-OMe (**2c**)	ZnCl	1	77 (**9**)
H (**2a**)	SnBu$_3$	0.5	91 (**8**)

Nevertheless, the Sonogashira coupling reaction, which avoided the preparation of stannylated reagents or Zn derivatives and which used a commercially available alkyne, was the most useful way to introduce a triple bond on η^5 manganese complexes, the yield being 79%. Thus, this reaction was extended to other alkynes.

We used mild conditions[15] in order to preserve the metallic fragment during the course of the reaction (Table 5). Complex **2a** reacted with trimethylsilylacetylene in the presence of Pd$_2$dba$_3$ and AsPh$_3$ at 35 °C in NEt$_3$ for 7 h to afford complex **10a** in 40% yield. The same reaction performed with complex **2c** delivered the coupling product **10c** in 78% yield.

To study the influence of the chlorine position in the π-system for the efficiency of introducing the triple bond, a Stille reaction was performed with another regioisomer: η^5-(2-chlorocyclohexadienyl)Mn(CO)$_3$ (eq 7). Complex **3b** reacted with tributylstannyl ethynylbenzene in

(14) Jackson, J. D.; Villa, S. J.; Bacon, D. S.; Pike, R. D.; Carpenter, G. B. *Organometallics* **1994**, *13*, 3972.
(15) Ravikanth, M.; Stachan, J. P.; Li, F.; Lindsey, J. S. *Tetrahedron* **1998**, *54*, 7721.

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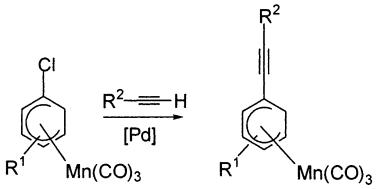
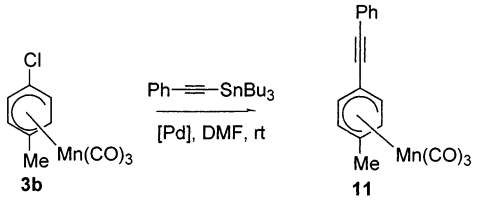
Table 5. Sonogashira Coupling Reaction with Complexes 2



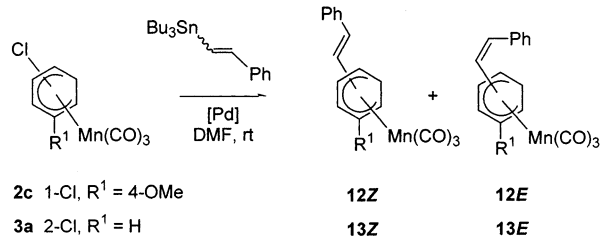
R^1 (complex)	R^2	complex (yield %)
H (**2a**)	$SiMe_3$	**10a** (40)
4-OMe (**2c**)	$SiMe_3$	**10c** (78)

DMF at room temperature for 30 min to deliver complex **11** in 95% yield. Thus, for the introduction of a triple bond, no kinetic difference between regioisomers (1-chlorocyclohexadienyl)$Mn(CO)_3$ **2** and (2-chlorocyclohexadienyl)$Mn(CO)_3$ **3** was noticed. No satisfactory explanation has been found yet.



(7)

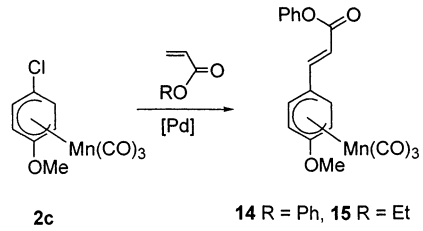
The synthesis of η^5-(cyclohexadienyl)$Mn(CO)_3$ substituted by a double bond could be achieved by Stille or Heck reactions. For the former, we used tributylstyrylstannane, prepared by hydrostannylation of phenylacetylene[16] as an equimolar mixture of isomers *Z* and *E*. Complex **2c** reacted smoothly with tributylstyrylstannane in DMF at room temperature in the presence of Pd_2dba_3 and $AsPh_3$ to afford after 24 h the expected coupling product **12** as a mixture of isomers *Z* and *E*, which could be separated by silica gel flash chromatography. Complexes **12*Z*** and **12*E*** were obtained in 31 and 32% yield, respectively (eq 8).



(8)

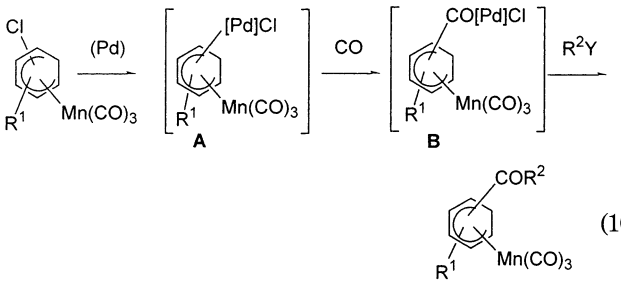
The same coupling reaction performed starting from η^5-(2-chlorocyclohexadienyl)$Mn(CO)_3$ **3a** evolved slowly (3 days) to give complexes **13** in 29% yield as an inseparable mixture of *Z* and *E* isomers (eq 8). Their 1:1 ratio was determined by NMR, confirming the preservation of the original isomer ratio as already observed for complex **12**. Moreover, as we have already observed for arylation processes, regioisomer (1-chlorocyclohexadienyl)$Mn(CO)_3$ **2** is much more reactive than (2-chlorocyclohexadienyl) $Mn(CO)_3$ **3**.

To complete this study of palladium-catalyzed reactions of η^5-(chlorocyclohexadienyl)$Mn(CO)_3$ with olefins, we turned our attention to Heck type reactions. We chose acrylate as a coupling partner. Complex **2c** reacted with phenylacrylate to afford complex **14** in 18% yield (eq 9). Application of Jeffery conditions by addition of a quaternary ammonium salt[17] did not allow us to improve the yield. Using ethyl acrylate, complex **15** was isolated in a modest 13% yield.



(9)

Carbonylation Reactions. The success of the coupling reactions prompted us to investigate the fate of these reactions under carbon monoxide atmosphere. Formation of intermediate **A** by Pd insertion in the C−Cl bond was established in the last sections (eq 10). CO insertion on complex **A** would give access to the acylpalladium **B**, whose trapping by various nucleophiles could lead to η^5-(cyclohexadienyl)$Mn(CO)_3$ complexes substituted by resonance-withdrawing groups, which were hitherto unknown in the literature (eq 10).



(10)

Three types of nucleophiles have been used: stannyl derivatives for the preparation of ketones, classical nucleophiles such as alcohol, amine, and thiol for the synthesis of carboxylic acid derivatives, and alkynes or alkenes to introduce yne-one or ene-one fragments. Carbonylation reactions were performed under CO atmosphere, using the previously described protocol. All experimental steps were accompanied by significant coloration changes of the solution from bright yellow to brown after addition of the catalyst. This color progressively disappeared, turning clear yellow. This change was attributed to the beginning of the oxidative addition.[18]

We first studied the catalyzed carbonylation of a series of η^5-(chlorocyclohexadienyl)$Mn(CO)_3$ **2** under CO atmosphere in the presence of Pd_2dba_3, $AsPh_3$, and stannous derivatives as a source of the second nucleophile R^2Y (Table 6).

Reaction of η^5-(1-Cl-4-Me-cyclohexadienyl)$Mn(CO)_3$ **2b** and 2-tributylstannylthiophene gave the thienyl ketone **16b** in 90% yield after refluxing the reaction mixture for 2 h (Table 6, entry 1). In the case of complex

(16) Zhang, H. X.; Guibé, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857.

(17) Jeffery, T. *Tetrahedron* **1996**, *52*, 10113.

(18) During all these processes reaction mixtures have to be kept carefully under CO atmosphere in order to avoid the formation of direct coupling compounds as byproducts. Auffrant, A.; Prim, D.; Rose-Munch, F.; Rose, E.; Vaissermann, J. *Organometallics* **2001**, *20*, 3214.

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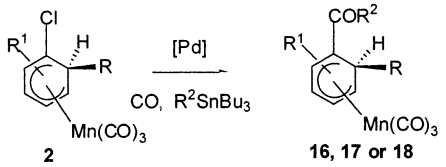
Table 6. Synthesis of Keto-Substituted η^5-(Cyclohexadienyl)Mn(CO)$_3$ Complexes



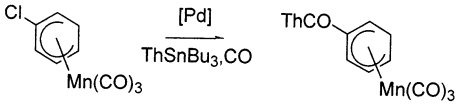
2 **16, 17 or 18**

entry	R^1	R	complex	R^2	reaction time (h)	complex (yield %)
1	4-Me	H	**2b**	Th	2	**16b** (90)
2	4-OMe	H	**2c**	Th	3	**16c** (92)
3	4-OMe	Ph	**2f**	Th	3	**16f** (73)
4	4-Me	H	**2b**	Bu	2	**17b** (56)
5	4-OMe	H	**2c**	Bu	2.5	**17c** (45)
6	4-OMe	Ph	**2f**	Me	24	**18** (69)
7	2-Me	H	**2d**	Th	18	**16d** (26)
8	4-OMe	H	**2c**	H		

2c the ketone **16c** was isolated in a similar yield (Table 6, entry 2). The same reaction could be performed with complex **2f**, whose sp^3 carbon is substituted by a phenyl group, to give complex **16f** in 73% yield (Table 6, entry 3).

This strategy has been extended to other stannous derivatives for the synthesis of alkyl ketones. Using $SnBu_4$ as nucleophile starting from complexes **2b** and **2c**, compounds **17b** and **17c** were obtained in 56 and 45% yield, respectively (Table 6, entries 4, 5). The same reaction was performed with complex **2f** and Me_4Sn to afford methyl ketone **18** in 69% yield (Table 6, entry 6). Thus no steric hindrance occurred in the case of complex **2f**. This is undoubtedly due to the distance between the phenyl substituent on the sp^3 carbon and the C_1 carbon, where the reaction took place. Reaction efficiency is affected by the presence of the *ortho* substituent with respect to the chlorine atom. Indeed in the case of complex **2d**, the carbonylation product was isolated in only 26% yield (Table 6, entry 7). It is worthy to note that complex **2c** reacting with Bu_3SnH did not allow the formation of the expected carboxaldehyde (Table 6, entry 8). We have not yet succeeded in the preparation of the aldehyde by changing the hydride source.

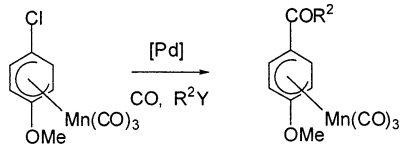
The regioisomer η^5-(2-chlorocyclohexadienyl)Mn(CO)$_3$ **3a** reacted much slower with ThSnBu and gave the corresponding ketone **19** in 70% yield after 2 days (eq 11).



3a **19** (11)

As the carbonylation process may involve the acylpalladate species **B** (eq 10), these reactions could be extended to carboxylic acid derivatives by trapping intermediate **B** with alcohols, amines, and thiols (Table 7). PhOH as well as MeOH reacted with complex **2c** in basic media to afford esters **20** in 71% yield and **21** (Table 7, entries 1 and 2). This latter complex exhibited a high degree of unstability and was used without any purification for further reactions. Carbonylation in the presence of morpholine and *p*-tolylthiol led to amide **22** and thioester **23** in 48 and 22% yield, respectively (Table 7, entries 3 and 4).

Table 7. Synthesis of η^5-(Cyclohexadienyl)Mn(CO)$_3$ Substituted by Carboxylic Acid Derivatives

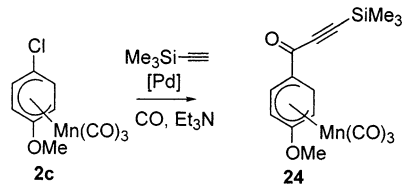


2c **20, 21, 22 or 23**

entry	R^2Y	base	R^2	complex (yield %)
1	PhOH	NaH	OPh	**20** (71)
2	MeOH	Et_3N	OMe	**21**[a]
3	$NH(CH_2CH_2)_2O$	K_2CO_3	$N(CH_2CH_2)_2O$	**22** (48)
4	*p*-tolylSH	NaH	*p*-tolylS	**23** (22)

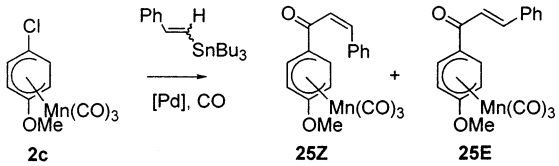
[a] Not isolated.

Taking advantage of the easy substitution of the chlorine atom by alkene, alkyne, and carbonyl functionalities, we were interested in associating these different procedures to synthesize yne- or ene-ones. We performed Sonogashira reactions under CO atmosphere in order to obtain yne-ones. Complex **24** was isolated in 74% yield by reacting complex **2c** and trimethylsilylacetylene in the presence of $Pd_2dba_3/AsPh_3$ in NEt_3 at 40 °C (eq 12).



2c **24** (12)

The same strategy applied to vinylstannane could lead to ene-ones. Thus, carbonylation of complex **2c** was performed in the presence of tributylstyrylstannane in THF using the same catalytic system. Complex **25** was isolated as *Z* and *E* isomers in 27 and 28% yield, respectively (1:1 ratio) (eq 13).



2c **25Z** **25E** (13)

We then tried the substitution of the chlorine atom by carbon- or heteroatom-based nucleophiles after the palladium oxidative addition. Such reactions performed with aryliodide or bromide and more recently with aryl chloride are reported in the literature as requiring the use of an elaborated catalytic system with bulky and electron-rich ligands.[19−21] In our case, we investigated the formation of a C−C bond between an sp^2 carbon of the cyclohexadienyl moiety and an sp^3 carbon of a nucleophile. Before paying attention to Pd-catalyzed processes, we ascertained that this reaction could not be achieved by direct nucleophilic substitution. It has

(19) Fox, J. M.; Huang, X.; Chieffi, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 1360, and references therein.
(20) Moradi, W. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, *123*, 7996, and references therein.
(21) Lee, S.; Beare, N. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 8410.

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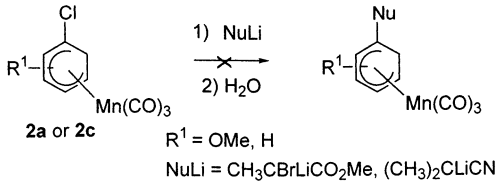
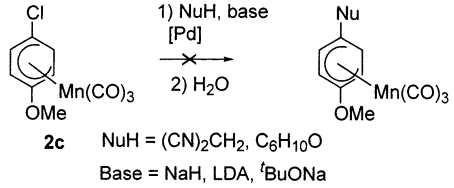
been well established[5c] that stabilized anions add to unsubstituted η^5-(cyclohexadienyl)$Mn(CO)_3$ complexes to give cyclohexadienes. We thought that in the presence of a leaving group (for example Cl^-) a substitution might take place. Unfortunately, using 2-bromomethylpropanoate or 2-isobutyronitrile anion as nucleophile and complex **2a** or **2c** as substrate, no reaction took place (eq 14).



(14)

To overcome this hurdle, a Pd-catalyzed alternative strategy was envisioned and, in particular, could the same catalytic system $Pd_2dba_3/AsPh_3$ be used to solve the problem encountered during direct substitution?

We used nucleophiles such as anions of malonitrile and cyclohexanone, whose arylation has been reported in the literature.[19,20,22−27] Reaction of complex **2c** with malonitrile in the presence of NaH and the catalytic system $Pd_2dba_3/AsPh_3$ at room temperature or at reflux failed. In the case of cyclohexanone two different bases were tested to generate the enolate: ^{t}BuONa or LDA. In both cases under THF reflux no coupling product was obtained (eq 15).

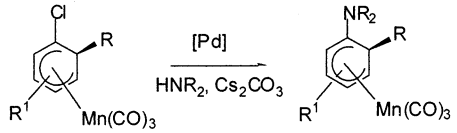


(15)

We then turned our attention to the Negishi reaction, where we were first interested in introducing a benzyl substituent. Benzylzinc bromide was prepared following literature procedure.[28] Reaction of complex **2c** and zinc reagent at THF reflux did not allow the isolation of a coupling product. Even the more nucleophilic methylpropanoatezinc iodide gave no reaction after several days at reflux in THF.

Finally a nitrile function could be introduced in an η^5-(cyclohexadienyl)$Mn(CO)_3$, by a palladium-catalyzed nucleophilic substitution of chlorine by nitrile.[29] Indeed potassium nitrile in the presence of the catalytic system ($Pd_2dba_3/AsPh_3$) and 18c6 crown ether in DMF

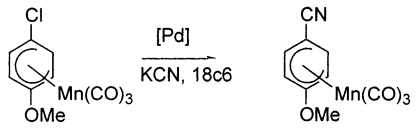
Table 8. Amination of η^5-(1-Chlorocyclohexadienyl)$Mn(CO)_3$ Complexes



2 **27, 28 or 29**

entry	R^1,R	complex	HNR_2	complex (yield %)
1	H, H	**2a**	morpholine	**27a** (84)
2	H, H	**2a**	morpholine	
3	4-Me, H	**2b**	morpholine	**27b** (76)
4	4-OMe, H	**2c**	morpholine	**27c** (90)
5	2-OMe, H	**2e**	morpholine	**27e**
6	4-OMe, 6-Ph	**2f**	morpholine	**27f** (55)
7	4-OMe, H	**2c**	$HNEt_2$	**28** (84)
8	4-OMe, H	**2c**	$H_2NCH(CH_3)Ph$	
9	4-Me, H	**2b**	$H_2N(C_6H_4)OMe$	**29** (42)

at 60 °C gave the expected nitrile compound **26** after 8 h[30] (eq 16).



(16)

We next turned our attention to N-, O-, S-, and P-based nucleophiles.[33] Results of amination reaction with η^5-(chlorocyclohexadienyl)$Mn(CO)_3$ complexes are gathered in Table 8. Reaction of complex **2a** with morpholine in the presence of Cs_2CO_3 and the catalytic system yielded complex **27a** in 84% yield (Table 8, entry 1). No reaction took place when the same reaction was conducted in the absence of a catalytic Pd system. Extending this strategy to various substituted η^5-(chlorocyclohexadienyl)$Mn(CO)_3$ complexes **2**, we studied the influence of substituents R^1 and R on the catalytic process. We observed that whatever the nature of R^1 and R, the reaction was efficient, providing that R^1 was a *para* substituent (entries 2, 3, 4, 6). Indeed when R^1 = 2-OMe, no reaction was observed (entry 5). Reaction took place even when C_6 was substituted by a phenyl group (entry 6).

Complex **2c** underwent coupling reaction with acyclic secondary amine (entry 7). This strategy could also be extended to primary amines but only in the case of aromatic amine such as anisidine (entry 9). In the case of methylbenzylamine a mixture of products impossible to analyze was obtained (entry 8).

The same reactions were performed with O-, S-, and P-based nucleophiles (Table 9). Preformed sodium phenolate and isoamylate reacted with complex **2c** to afford ethers **30** and **31** in 31 and 38% yield, respectively (Table 9, entries 1, 2).

Thioethers **32** and **33** could also be synthesized under the same reaction conditions using either aliphatic or aromatic thiolates (Table 9, entries 3−5, 7). As we

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(22) Uno, M.; Seto, K.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 932.
(23) Shaughnessy, K. H.; Hamann, B. C.; Hartwig, J. P. *J. Am. Chem. Soc.* **1998**, *63*, 6546.
(24) Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 1108.
(25) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 12382.
(26) Ahnman, J.; Wolfe, J. P.; Troutman, M. V.; Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 1918.
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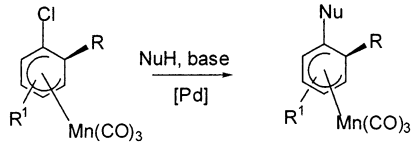
(28) Rottländer, M.; Knochel, P. *Tetrahedron Lett.* **1997**, *38*, 1749.
(29) Sundermeier, M.; Zapf, A.; Beller, M.; Sans, J. *Tetrahedron Lett.* **2001**, *421*, 6707.
(30) This compound could not be isolated because of its sensitivity to silica; this is the reason it was used without purification for rearomatisation.
(31) Xu, Y.; Li, Z.; Xia, J.; Guo, H.; Huang, Y. *Synthesis* **1984**, 781.
(32) Prim, D.; Campagne, J. M.; Joseph, D.; Andrioletti, B. *Tetrahedron* **2002**, *58*, 2041.
(33) Auffrant, A.; Prim, D.; Rose-Munch, F.; Rose, E.; Vaissermann, J. *Organometallics* **2002**, *21*, 3500.

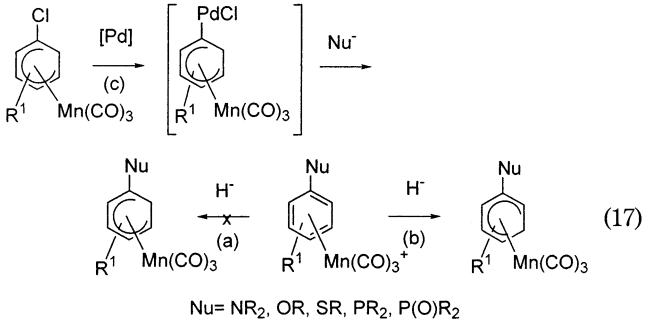
Table 9. Substitution of η^5-(1-Chlorocyclohexadienyl)Mn(CO)$_3$ Complexes by Ether, Thio-ether, Phosphine Oxide, and Phosphino Groups



2 **30-36**

entry	R¹, R	complex	NuH	complex (yield %)
1	4-OMe, H	**2c**	PhOH	**30** (31)
2	4-OMe, H	**2c**	isoamylOH	**31** (38)
3	4-OMe, H	**2c**	$C_5H_{14}SH$	**32** (73)
4	H, H	**2a**	*p*-tolylSH	**33a** (86)
5	4-OMe, H	**2c**	*p*-tolylSH	**33c** (93)
6	2-OMe, H	**2e**	*p*-tolylSH	**33e**
7	4-OMe, Ph	**2f**	*p*-tolylSH	**33f** (88)
8	4-OMe, H	**2c**	$HP(O)(OEt)_2$	**34** (77)
9	4-OMe, H	**2c**	$HP(O)(Ph)_2$	**35** (43)
10	4-OMe, H	**2c**	$HP(Ph)_2$	**36** (64)

already observed with amines, the presence of an *ortho* substituent precluded any reaction (entry 6), whereas a substituent at C_6 did not decrease the reaction efficiency (entry 7). Introduction of P-based nucleophiles was achieved using triethylamine as a base instead of NaH as previously described.[31] Derivatives of diethyl phosphite **34**, diphenyl phosphine oxide **35**, and diphenylphosphine **36** were isolated in 77, 43, and 64% yield (entries 8−10). In the case of complex **35**, performing the reaction in DMF at 50 °C instead of THF reflux increased the yield (43% vs 36%). Thus the preparation of unprecedented η^5-(1-Nu-cyclohexadienyl)Mn(CO)$_3$ complexes was realized by an overall palladium-catalyzed substitution of the chlorine atom. Since electron-releasing groups exclusively direct *meta* addition (eq 17, path b), such complexes cannot be prepared by hydride addition onto η^6-(Nu-arene)Mn(CO)$_3^+$ (eq 17, path a). In our case, the use of a Buchwald-Hartwig type strategy starting from η^5-(1-Cl-cyclohexadienyl)Mn(CO)$_3$ complexes gave a selective access to η^5-(1-Nu-cyclohexadienyl)Mn(CO)$_3$ complexes (eq 17, path c).



(17)

Nu= NR_2, OR, SR, PR_2, $P(O)R_2$

Moreover, in contrast with organic compounds series which require a sophisticated catalytic system,[32] synthesis of η^5-(cyclohexadienyl)Mn(CO)$_3$ bearing a donor group at the end of the π-system was achieved by palladium-catalyzed reactions using the same nonelaborated catalytic system $Pd_2dba_3/AsPh_3$.[33]

X-ray Analysis of the η^5-(1-R²-Cyclohexadienyl)-Mn(CO)$_3$ Complexes. X-ray studies were undertaken for each type of coupling products. Crystals of η^5-tricarbonylmanganese complexes **23** and **33f** were grown in a diethyl ether/hexane mixture (Figures 2, 3 and Table 10). Some selected bond lengths and dihedral angles are presented in Table 11 as well as those of complexes **5b**[9c] and **33c**[33] (Figure 4) for comparison. Two important features can be emphasized. First they generally confirm the η^5 structure of the coupling product: we observe, as usually described,[34−37] five coplanar sp^2 carbons, while the remaining sp^3 carbon is located out of this plane away from the metal. The dihedral angles between $[C_1C_6C_5]$ and $[C_1C_2C_3C_4C_5]$ planes reported in Table 11 are in good agreement with literature data (except for **33c**, vide infra).

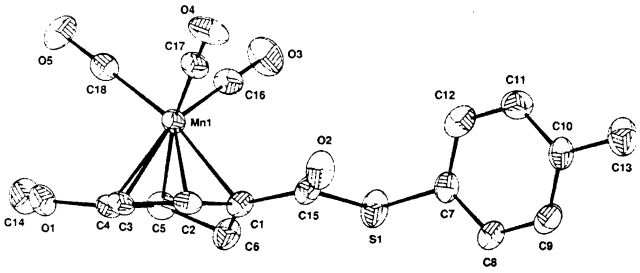


Figure 2. ORTEP views of complex **23** (thermal ellipsoids are at 30% probability).

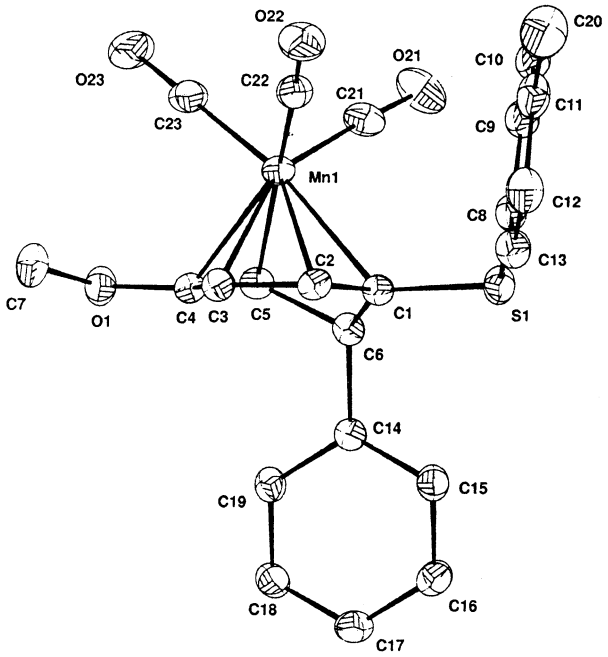


Figure 3. ORTEP views of complex **33f** (thermal ellipsoids are at 30% probability).

The second point concerning X-ray structures presented in Figures 2 and 3 is the evidence of the regioselective "*ipso*" process of the Pd-catalyzed reaction. Indeed, the incoming R^2 substituent is located at C_1, which previously bore the chlorine atom. For all these structures the conformation of the Mn(CO)$_3$ tripod is in agreement with what is usually observed: the sp^3

(34) Lee, T. Y.; Bae, H. K.; Chung, Y. K.; Hallows, W. A.; Sweigart, D. A. *Inorg. Chim. Acta* **1994**, *224*, 147.
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Table 10. Crystal Data for 23, 33f, 40c, and 44

	23	33f	40c	44
formula	$C_{18}H_{15}MnO_5S$	$C_{23}H_{19}MnO_4S$	$C_{16.5}H_{13}BF_4MnO_{5.5}S$	$C_{16}H_{16}BF_4MnO_5Si$
fw (g mol^{-1})	398.3	446.39	473.07	458.12
a (Å)	7.019(7)	9.544(2)	21.279(19)	10.481(4)
b (Å)	14.076(19)	9.944(2)	14.729(4)	18.840(4)
c (Å)	19.066(16)	12.405(2)	13.782(4)	10.618(2)
α (deg)	72.55(10)	101.63(1)	90	90
β (deg)	79.45(7)	109.21(2)	113.86(6)	93.74(3)
γ (deg)	89.85(9)	103.93(2)	90	90
V (Å^3)	1764(4)	1027.2(4)	3950(4)	2092(1)
Z	4	2	8	4
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/a$
abs μ (cm^{-1})	8.56	7.4	8.05	7.2
density ρ (g cm^{-3})	1.50	1.44	1.59	1.45
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan range (deg)	$0.8 + 0.345 \tan\theta$	$0.8 + 0.345 \tan\theta$	$0.8 + 0.345 \tan\theta$	$0.8 + 0.345 \tan\theta$
θ limits (deg)	1−25	1−28	1−25	1−26
h,k,l limits	0,8; −16,16; −22,22	0,12; −13,12; −16,15	0,25; 0,17; −16,14	0,12; 0,23; −13,13
no. data collected	6768	5236	3789	4467
no. unique data	6211 ($R_{int} = 0.05$)	4942 ($R_{int} = 0.02$)	3475 ($R_{int} = 0.04$)	4093 ($R_{int} = 0.01$)
no. data used	3187 ($I > 3\sigma(I)$)	4053 ($I > 3\sigma(I)$)	1579 ($I > 3\sigma(I)$)	2384 ($I > 3\sigma(I)$)
R^a	0.0634	0.0369	0.11	0.0534
$R_w{}^b$	0.0730	0.0455	0.13	0.0639
GOF	1.08	1.04	1.08	1.07
no. variables	452	264	229	255
$\Delta\rho_{min}$ (e Å^{-3})	−0.85	−0.38	−0.73	−0.41
$\Delta\rho_{max}$ (e Å^{-3})	1.04	0.44	1.37	0.46
(shift/esd)$_{max}$	0.029	0.00077	0.179	0.057

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

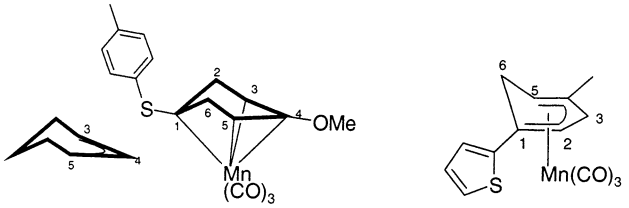

Figure 4. "High-heeled shoe" conformation complex **33c** and complex **5b**.

Table 11. Selected Bond Lengths (Å) and Dihedral Angles (deg) of Complexes 5b, 23, 33c, and 33f

	5b	23	33c	33f
Mn−C_1	2.268	2.173	2.172	2.268
Mn−C_2	2.138	2.117	2.385	2.138
Mn−C_3	2.120	2.148	2.153	2.124
Mn−C_4	2.154	2.204	2.198	2.168
Mn−C_5	2.203	2.224	2.2167	2.156
[$C_1C_6C_5$]/[$C_1C_2C_3C_4C_5$]	40	40	25	40

carbon is eclipsed by one Mn−CO bond.[34−37] It is also worthy to note that the Mn−C_3 bond is the shortest Mn-cyclohexadienyl bond length (except for complex **23**). The carbonyl function of **23** (Figure 2) is not in the cyclohexadienyl plane but deviated by 18° toward the $Mn(CO)_3$ entity. The structure of **33c** (Figure 4) is particularly surprising since the five carbons of the cyclohexadienyl moiety are not coplanar.[33] Indeed carbons C_2 and C_6 are located out of the plane formed by C_1, C_3, C_4, and C_5 away from the metal. Dihedral angles between [C_1, C_2, C_3] and [C_1, C_5, C_6] with [C_1, C_3, C_4, C_5] planes have very close values: 19.8° for the first one and 25.2° for the second. This has been viewed as a π-allyl C_3, C_4, C_5 σ-alkyl C_1 derivative[38] which might be represented by "a high-heeled shoe" conformation.

This unprecedented structure is not observed for **33f** (Figure 3), which differs from **33c** by the presence of a phenyl substituent on the sp^3 carbon. In this case, the classical η^5 feature with five coplanar carbons is observed. The phenyl substituent is almost orthogonal to the cyclohexadienyl plane, making a dihedral angle of 86°. The sulfur substituent forms an angle of 96° with the cyclohexadienyl plane and of 79° with the phenyl substituent.

The position of the *p*-S-tolyl ring is very different for the two complexes. In **33f**, the ring is orthogonal to the [C_1, C_4, S] plane and oriented toward the $Mn(CO)_3$ moiety because of the presence of the sterically demanding phenyl substituent at the sp^3 C_6 carbon, and the sulfur atom is pointing in the direction opposite the manganese entity. On the contrary, in **33c**, the tolyl ring is oriented in the direction opposite the $Mn(CO)_3$ group and the sulfur atom is pointing toward the metal. This orientation could favor some interactions of the sulfur atom with the two symmetrical carbonyl groups (C_{21}−O_{21} and C_{22}−O_{22}) and could induce the deviation observed for C_2. It is worthy to note that, when the sulfur atom is one carbon away from the metal entity like in compound **23**, no interaction is possible and no deformation of the η^5-cyclohexadienyl plane is observed.

Synthesis of Novel Cationic η^6-(Arene)Mn(CO)$_3^+$ Complexes. As the functionalizations presented in the aforementioned section preserved the manganese fragment and kept the methylene carbons intact, all the conditions were gathered to try the rearomatization of the new η^5 complexes by *exo*-hydride abstraction. We first focused on the preparation of cationic η^6-(arene)-$Mn(CO)_3^+$ complexes conjugated with an aromatic system, a double or a triple bond. Such compounds are difficult or impossible to prepare selectively by direct complexation. For example, it is known that metalation

(38) σ,π-Cyclohexenyl complex reported by, Pike, R. D.; Ryan, W. J.; Lennhof, N. S.; Van Epp, J.; Sweigart, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 4798, is similar to that obtained here. But in this structure the carbon C_2 is effectively a sp^3 carbon not bonded to the metal center.

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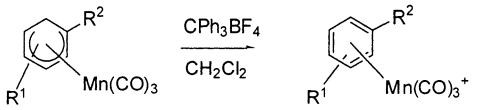
Table 12. Synthesis of New η^6-(Arene)Mn(CO)$_3^+$ Complexes



entry	complex	R^1, R^2	complex (yield %)
1	**5c**	4-OMe, Th	**37** (93)
2	**9**	4-OMe, C≡CPh	**38** (96)
3	**12*E***	4-OMe, CH=CHPh	**39*E*** (94)
4	**16b**	4-Me, COTh	**40b** (95)
5	**16c**	4-OMe, COTh	**40c** (95)
6	**20**	4-OMe, CO_2Ph	**41** (70)
7	**21**	4-OMe, CO_2Me	**42** (77, 2 steps)
8	**22**	4-OMe, $CO_2N[(CH_2)_2]_2O$	**43** (85)
9	**24**	4-OMe, $COC{\equiv}CSiMe_3$	**44** (65)
10	**26**	CN	**45** (35, 2 steps)

of 2-phenylpyrrole gave exclusively 2-phenyl-(η^5-pyrrolyl)tricarbonylmanganese[39] and that phenylacetylene could not be coordinated to the Mn(CO)$_3$ entity.[14] We were interested in preparing 2-thienyl-(η^6-anisole)Mn(CO)$_3^+$ by rearomatization of η^5(1-thienyl-4-methoxycyclohexadienyl)Mn(CO)$_3$ **5c**. The reaction with $CPh_3^+BF_4^-$ proceeded smoothly to deliver complex **37** in 93% yield (Table 12, entry 1). Similarly, complexes **9** and **12*E*** were subjected to rearomatization upon hydride abstraction, and complexes **38** and **39*E*** were isolated in 96 and 94% yield, respectively (Table 12, entries 2, 3).

Taking advantage of these precedents, we have turned our attention toward the synthesis of resonance withdrawing group substituted cationic complexes which were never described in the literature since the low electronic density of the aromatic cycle prevents any direct complexation.[14] Even disrupting the electron transfer to the acceptor group by protecting the electron-withdrawing substituent precludes metalation.[14] The coexistence of two strong electron-withdrawing groups, the carbonyl or the nitrile function and the metal entity Mn(CO)$_3^+$ on the arene, was an interesting challenge. Complexes **16b** and **16c** reacted with triphenylcarbenium tetrafluoroborate to deliver complexes **40b** and **40c** in excellent yield (95%) (Table 12, entries 4, 5). No problem of stability during the reaction or for the isolation of the products was observed. Cationic carboxylic acid derivatives (ester and amide) were obtained in the same way (Table 12, entries 6−8), even in the case of complex **42**, whose η^5 intermediate could not be isolated after the coupling reaction (entry 7). Yne-one **24** was successfully subjected to the same conditions to yield complex **44** (entry 9). Complex **45**, arising from hydride abstraction performed on the crude mixture containing **26** (entry 10), was obtained in 35% yield for the two steps. Thus, for the first time, it was possible to undertake studies on the tripod conformation of η^6-(EWG-arene)Mn(CO)$_3^+$ in solution by NMR and in the solid state by X-ray analysis. In the case of the complexes reported in Table 12, the difference of the chemical shifts of H^2 and H^3 proton resonances is, as expected, noticeable and can reach +1.2 ppm. This is due to the electronic distribution created by a resonance-withdrawing group (EWG = COTh, CO_2Ph, CO_2Me, $CON[(CH_2)_2]O$, $COCCSiMe_3$, CN) located *para* to an

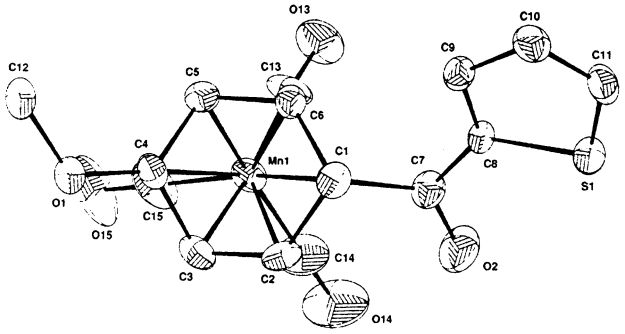


Figure 5. ORTEP views of complex**40c** (thermal ellipsoids are at 30% probability).

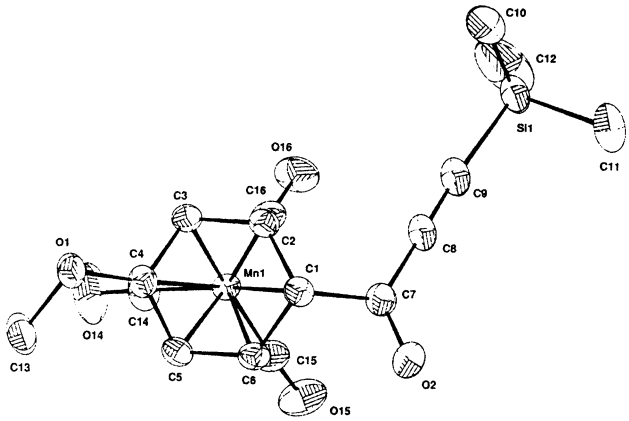
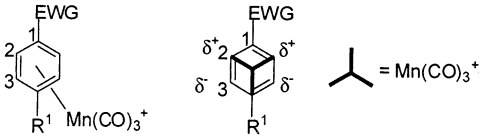


Figure 6. ORTEP views of complex **44 (**thermal ellipsoids are at 30% probability).

Table 13. H_2 and H_3 Chemical Shifts in η^6-(EWG-arene)Mn(CO)$_3^+$ Complexes



complex	R^1	EWG	$\delta(H_2)$	$\delta(H_3)$	$\Delta\delta = \delta(H_2) - \delta(H_3)$
40b	4-OMe	COTh	7.66	7.57	1.09
40c	4-Me	COTh	7.52	6.83	0.69
41	4-OMe	CO_2Ph	7.69	6.49	1.20
42	4-OMe	CO_2Me	7.64	6.56	1.08
43	4-OMe	$CON[(CH_2)_2]O$	7.43	6.40	1.03
44	4-OMe	$COCCSiMe_3$	7.78	6.59	1.19
45	4-OMe	CN	7.90	7.74	0.14

electron-donating group (R^1 = OMe, Me): it induces a positive charge on the C_2 carbon and a negative one on the C_3 carbon (Table 13). As a consequence, proton H^2 is deshielded whereas proton H^3 is shielded, leading to noticeable values of $\Delta\delta$ (up to 1.20 ppm versus an average 0.40 ppm value for non-substituted complexes). Such values of $\Delta\delta$ are in good agreement with an *anti*-eclipsed conformation of the Mn(CO)$_3$ tripod with respect to the electron-withdrawing group in solution (Table 13).[40]

The first study of the conformation of η^6-(EWG-arene)-Mn(CO)$_3^+$ in the solid state was allowed by X-ray analysis of complexes **40c** (Figure 5) and **44** (Figure 6). Selected bond lengths and angles are given in Table 14

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(40) For chromium analogues see: (a) Hoffmann, R.; Hoffmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598. (b) Rose-Munch, F.; Rose, E. *Curr. Org. Chem.* **1999**, *3*, 445.

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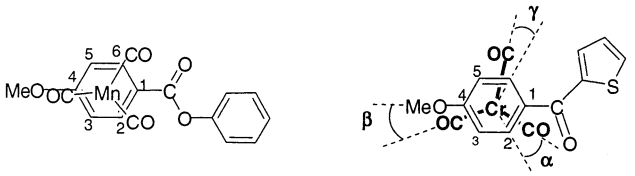

Figure 7. Complex **41** and complex **40Cr**.

Table 14. Selected Bond Lengths (Å) and Dihedral Angles (deg) of Complexes 40c, 41a, 41b, 44, 40Cr

	40c	41a	41b	44	40Cr
Mn−C_1	2.17	2.154	2.161	2.148	2.181
Mn−C_2	2.17	2.171	2.186	2.151	2.206
Mn−C_3	2.22	2.199	2.226	2.203	2.238
Mn−C_4	2.31	2.273	2.266	2.298	2.282
Mn−C_5	2.21	2.20	2.186	2.205	2.242
Mn−C_6	2.16	2.153	2.153	2.153	2.181
α (deg)	9	8	5	6	21
β (deg)	6	5	17	6	22
γ (deg)	9	2	14	5	22

together with those of complexes **41**[18] and **40Cr**[9b] (Figure 7), the related isoelectronic, neutral tricarbonylchromium complex, analogous to **40c**.

The cation displays the well-known piano stool conformation found in half-sandwich tricarbonyl complexes.[41] The arene-ring and C_7 carbon atoms were found almost coplanar. The Mn−C(ring) bond lengths ranging from 2.15 to 2.30 Å (average 2.20 Å) are a bit shorter than the corresponding distances in complex **40Cr** (average 2.23 Å).[42] The positive charge on the manganese atom results in a little contraction of the metal ring average distances. Moreover, comparison of the bond lengths collected in Table 14 shows that Mn−C_1, Mn−C_2, and Mn−C_6 distances are shorter than Mn−C_3, Mn−C_4, and Mn−C_5 ones. This is due to the manganese entity displacement from the center of the six arene carbons toward the C_1 carbon substituted by the carbonyl function.[43]

The conformation of the tripod is, for each complex, almost *anti*-eclipsed. Deviation of α, β, and γ angles reported in Table 14 are much smaller than those corresponding to complex **40Cr**, whose conformation has been reported as staggered.[9b]

For complex **40c** (Figure 5), the carbonyl function is out of the plane of the arene ring, pointing toward the metal with a dihedral angle of 31°. For the chromium complex **40Cr** (Figure 7), the carbonyl function pointed in the direction opposite the $Cr(CO)_3$ moiety.[9b]

In the X-ray analysis of complex **41**[18] we observed two independent molecular cations differing by the conformation of the tricarbonylmanganese tripod. In one of these complexes (represented in Figure 7) the structure showed an *anti*-eclipsed conformation with respect to the ester group, whereas in the other one, a slightly deviated conformation was observed. For the yne-one complex **44** (Figure 6), the methoxy group lies in the arene ring plane, whereas C_8, C_9 carbon atoms and the silicon atom are out of this plane, with respective distances of 0.11, 0.25, and 0.47 Å.

These first structures of η^6-(EWG-arene)$Mn(CO)_3^+$ complexes showed an *anti*-eclipsed conformation of the tripod with respect to the electron-accepting group. Such orientation was until now just a hypothesis by analogy with tricarbonylchromium complexes.

Conclusion

We successfully developed a general palladium-catalyzed strategy for unprecedented functionalization of η^5-(cyclohexadienyl)$Mn(CO)_3$ complexes. In particular, η^5 complexes bearing either electron-donating or -withdrawing groups at the terminus of the π-system were obtained in high yield. X-ray analysis of four η^5 complexes was also presented. The method of functionalization preserving the methylene *exo* fragment allows the rearomatization of the η^5 complex by hydride abstraction, leading to new cationic η^6-(arene)$Mn(CO)_3^+$ complexes. The first conformational studies of cationic arene tricarbonylmanganese complexes substituted by resonance-withdrawing groups were conducted in solution and in the solid state, evidencing an *anti*-eclipsed conformation with respect to the carbon bearing the electron acceptor substituents.

Experimental Section

All reactions and manipulations were routinely performed under a dry nitrogen atmosphere using Schlenk tube techniques. THF was dried over sodium benzophenone ketyl and distilled. Infrared spectra were measured on a Perkin-Elmer 1420 spectrometer. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AC200, AC400, or DRX500 spectrometer. Elemental analyses were performed by Le service de Microanalyses de l'Université Pierre et Marie Curie.

Preparation of η^6-(Chloroarene)$Mn(CO)_3^+$: 1. Complexes **1a**[4a] and **1b**−**1e**[7] were synthesized following procedures already described in the literature.

Preparation of η^5-(Chlorocyclohexadienyl)$Mn(CO)_3$: 2 and 3. Complexes **2a**,**b**, **3a**,**b**[4a] **2c**−**e**, and **3c**−**e**[7] were prepared by addition of $AlLiH_4$ as already described.

Complex **2f** was prepared by addition of phenylmagnesium bromide, with an experimental procedure similar to that described by Chung.[11] ^1H NMR ($CDCl_3$): 3.48 (3H, s, OMe), 3.56 (1H, dd, J = 6.5 and 3 Hz, H_5), 4.49 (1H, dd, J = 1.5 and 6.5 Hz, H_{6endo}), 5.21 (1H, dd, J = 1.5 and 6 Hz, H_2), 5.55 (1H, dd, J = 6 and 3 Hz, H_3), 6.99 (2H, t, J = 5 Hz, Ar H), 7.20 (3H, m, Ar H). ^{13}C NMR ($CDCl_3$): 45.1 (C_5), 52.2 (C_6), 54.9 (OMe), 64.5 (C_3), 80.0 (C_1), 92.5 (C_2), 126.1 (Ar CH), 127.7 (Ar CH), 128.6 (Ar CH), 141.7 (Ar C), 143.7 (C_4), 221.6 (CO(Mn)). Anal. Calcd: C, 53.63; H, 3.38. Found: C, 53.45; H, 3.20.

Stille Arylation of η^5-(Chlorocyclohexadienyl)$Mn(CO)_3$: 2 and 3. Typical Arylation Procedure: Preparation of Complex 4a. Pd_2dba_3 (0.029 g, 0.03 mmol) and $AsPh_3$ (0.034 g, 0.11 mmol) were added successively to complex **2a** (0.081 g, 0.32 mmol) in 7 mL of anhydrous degassed DMF. After 5 min at room temperature tributylstannylbenzene (0.104 mL, 0.32 mmol) was introduced. The mixture was stirred for 23 h at room temperature, poured into 50 mL of cold ice water, and extracted twice with 30 mL of pentane. The combined organic phases were washed with water (20 mL), dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The residue was then purified by flash chromatography on silica gel (pentane) to afford complex **4a** in 52% yield. IR ($CHCl_3$): 1914, 2003 (CO(Mn)). ^1H NMR ($CDCl_3$): 2.53 (1H, d, J = 13 Hz, H_{6exo}), 3.19 (1H, t, J = 6 Hz, H_5), 3.28 (1H, dd, J = 13 and 6 Hz, H_{6endo}), 5.02 (1H, t, J = 6 Hz, H_4), 5.29 (1H, d, J = 6 Hz, H_2), 5.98 (1H, t, J = 6 Hz, H_3), 7.41 (5H, m, Ar H). ^{13}C NMR ($CDCl_3$): 23.5 (C_6), 54.8 (C_5), 82.2 (C_3), 92.3 (C_2), 99.1 (C_4), 102.1 (C_1), 127.0 (Ar CH), 128.2

(41) Berndt, A. F.; Marsh, R. E. *Acta Crystallogr.* **1963**, *16*, 118.
(42) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.
(43) The same phenomena were observed for tricarbonylchromium complexes, see: Djukic, J. P.; Rose-Munch, F.; Rose, E.; Vaissermann, J. *Eur. J. Inorg. Chem.* **2000**, 1295.

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(Ar CH), 130.5 (Ar CH), 133.1 (Ar C), 222.7 (CO(Mn)). Anal. Calcd: C, 61.24; H, 3.77. Found: C, 59.97; H, 3.84.

Performing the same reaction using $SbPh_3$ instead of $AsPh_3$ allows the isolation of complex **4′a** (20%) together with **4a** (60%). **4′a** IR ($CHCl_3$): 1994, 2058 (CO(Mn)), 1600 (CO). ^{1}H NMR ($CDCl_3$): 2.15 (1H, d, J = 14 Hz, H_{6exo}), 3.41 (1H, dd, J = 14 and 6 Hz, H_{6endo}), 3.51 (1H, dd, J = 6 and 3 Hz, H_5), 5.09 (1H, t, J = 3 Hz, H_4), 5.29 (1H, d, J = 3 Hz, H_2), 5.98 (1H, t, J = 3 Hz, H_3), 7.44 (5H, m, Ar H). Anal. Calcd: C, 59.64; H, 3.44. Found: C, 59.63; H, 3.44.

Complex **4b** was obtained by the same procedure using $AsPh_3$ as ligand in 45% yield. IR ($CHCl_3$): 1916, 1996 (CO(Mn)). ^{1}H NMR ($CDCl_3$): 1.91 (3H, s, Me), 2.13 (1H, d, J = 13 Hz, H_{6exo}), 3.04 (1H, m, H_{6endo}), 3.25 (1H, m, H_5), 5.22 (1H, d, J = 6 Hz, H_2), 5.82 (1H, d, J = 6 Hz, H_3), 7.35 (5H, m, Ar H). ^{13}C NMR ($CDCl_3$): 22.7 (Me), 32.5 (C_6), 52.1 (C_5), 76.2 (C_1), 94.0 (C_3), 95.8 (C_2), 110.3 (C_4), 127.9 (Ar CH), 128.4 (Ar CH), 130.1 (Ar CH), 133.1 (Ar C), 223.4 (CO(Mn)). Anal. Calcd: C, 62.35; H, 4.25. Found: C, 62.54; H, 4.01.

Arylation procedure performed with tributylstannylthiophene instead of tributylstannylbenzene afforded complexes **5**. Complex **5a** was isolated in 51% yield. IR ($CHCl_3$): 1915, 2000 (CO(Mn)). ^{1}H NMR ($CDCl_3$): 2.45 (1H, d, J = 13 Hz, H_{6exo}), 3.21 (2H, m, H_5, H_{6endo}), 4.95 (1H, t, J = 5 Hz, H_4), 5.25 (1H, d, J = 5 Hz, H_2), 5.86 (1H, t, J = 5 Hz, H_3), 6.86 (1H, d, J = 4 Hz, Ar H), 6.94 (1H, m, Ar H), 7.17 (1H, d, J = 5 Hz, Ar H). ^{13}C NMR ($CDCl_3$): 28.7 (C_6), 51.2 (C_5), 77.6 (C_3), 94.5 (C_2), 97.2 (C_4), 103.1 (C_1), 122.6 (Ar CH), 125.1 (Ar CH), 128.0 (Ar CH), 133.7 (Ar C), 226.1 (CO(Mn)). Anal. Calcd: C, 52.00; H, 3.00. Found: C, 52.12; H, 2.80.

5b (48%). IR ($CHCl_3$): 1917, 1998 (CO(Mn)). ^{1}H NMR ($CDCl_3$): 1.90 (3H, s, Me), 2.51 (1H, d, J = 12 Hz, H_{6exo}), 3.15 (1H, d, J = 6 Hz, H_5), 3.24 (1H, dd, J = 6 and 12 Hz, H_{6endo}), 5.22 (1H, d, J = 6 Hz, H_2), 5.74 (1H, d, J = 6 Hz, H_3), 6.84 (1H, d, J = 4 Hz, Ar H), 6.92 (1H, m, Ar H), 7.15 (1H, d, J = 4 Hz, Ar H). ^{13}C NMR ($CDCl_3$): 21.9 (Me), 29.3 (C_6), 50.8 (C_5), 77.9 (C_3), 94.1 (C_2), 97.8 (C_4), 106.2 (C_1), 122.3 (Ar CH), 124.8 (Ar CH), 127.7 (Ar CH), 133.8 (Ar C), 223.2 (CO(Mn)). Anal. Calcd: C, 53.51; H, 3.53. Found: C, 53.59; H, 3.75.

5c (78%). IR ($CHCl_3$): 1922, 1990 (CO(Mn)). ^{1}H NMR ($CDCl_3$): 2.60 (1H, d, J = 13 Hz, H_{6exo}), 3.10 (1H, m, H_5), 3.29 (1H, m, H_{6endo}), 3.51 (3H, s, OMe), 5.27 (1H, d, J = 6 Hz, H_2), 5.76 (1H, d, J = 6 Hz, H_3), 6.80 (1H, d, J = 3.5 Hz, Ar H), 6.91 (1H, dd, J = 3.5 and 4.5 Hz, Ar H), 7.14 (1H, d, J = 4.5 Hz, Ar H). ^{13}C NMR ($CDCl_3$): 29.5 (C_6), 35.6 (C_5), 53.4 (OMe), 63.3 (C_1), 65.5 (C_3), 106.2 (C_2), 121.2 (Ar CH), 123.5 (Ar CH), 126.5 (Ar CH), 132.7(Ar C), 143.0 (C_4), 224.3 (CO(Mn)). Anal. Calcd: C, 50.92; H, 3.36. Found: C, 50.80; H, 3.41.

5d (53%). IR ($CHCl_3$): 1917, 1998 (CO(Mn)). ^{1}H NMR ($CDCl_3$): 2.02 (3H, s, Me), 2.60 (1H, d, J = 12 Hz, H_{6exo}), 3.06 (2H, m, H_{6endo}, H_5), 4.87 (1H, t, J = 5 Hz, H_4), 5.75 (1H, d, J = 5 Hz, H_3), 6.82 (1H, d, J = 4 Hz, Ar H), 6.94 (1H, m, Ar H), 7.20 (1H, d, J = 5 Hz, Ar H). ^{13}C NMR ($CDCl_3$): 19.6 (Me), 31.7 (C_6), 49.7 (C_5), 75.1 (C_2), 79.5 (C_3), 94.7 (C_4), 105.4 (C_1), 123.8 (Ar CH), 125.7 (Ar CH), 127.6 (Ar CH), 132.6 (Ar C), 222.2 (CO(Mn)). Anal. Calcd: C, 53.51; H, 3.53. Found: C, 53.57; H, 3.66.

Similar arylation reaction starting from complexes **3** led to complexes **6**. **6a** (58%). IR ($CHCl_3$): 1915, 2000 (CO(Mn)). ^{1}H NMR ($CDCl_3$): 2.17 (1H, d, J = 14 Hz, H_{6exo}), 2.83 (1H, m, H_{6endo}), 2.99 (1H, m, H_5), 3.42 (1H, m, H_1), 4.93 (1H, m, H_4), 6.35 (1H, dd, J = 6 and 3 Hz, H_3), 6.97 (1H, d, J = 4 Hz, Ar H), 7.22 (2H, m, Ar H). ^{13}C NMR ($CDCl_3$): 29.7 (C_6), 52.4 (C_5), 77.2 (C_3), 78.0 (C_1), 92.7 (C_4), 116.8 (C_2), 122.1 (Ar CH), 124.5 (Ar CH), 127.5 (Ar CH), 132.9 (Ar C), 223.0 (CO(Mn)). Anal. Calcd: C, 52.00; H, 3.00. Found: C, 52.25; H, 3.05.

6b (30%). IR ($CHCl_3$): 1920, 1998 (CO(Mn)). ^{1}H NMR ($CDCl_3$): 1.61 (3H, s, Me), 2.35 (1H, d, J = 14 Hz, H_{6exo}), 2.76 (1H, dd, J = 6 and 14 Hz, H_{6endo}), 3.36 (1H, d, J = 6 Hz, H_1), 4.65 (1H, d, J = 5 Hz, H_4), 6.18 (1H, d, J = 5 Hz, H_3), 6.95 (1H, d, J = 4 Hz, Ar H), 7.21 (2H, m, Ar H). ^{13}C NMR ($CDCl_3$): 21.6 (Me), 30.1 (C_6), 51.0 (C_5), 70.7 (C_1), 74.9 (C_3), 95.8 (C_4), 115.1 (C_2), 121.9 (Ar CH), 124.8 (Ar CH), 128.1 (Ar CH), 133.2 (Ar C), 222.4 (CO(Mn)). Anal. Calcd: C, 53.51; H, 3.53. Found: C, 53.6; H, 3.69.

6d (43%). IR ($CHCl_3$): 1919, 1997 (CO(Mn)). ^{1}H NMR ($CDCl_3$): 1.88 (3H, s, Me), 2.38 (1H, d, J = 13 Hz, H_{6exo}), 2.75 (1H, m, H_{6endo}), 2.99 (1H, m, H_5), 4.83 (1H, m, H_4), 6.01 (1H, d, J = 6 Hz, H_3), 6.97 (1H, d, J = 4 Hz, Ar H), 7.19 (2H, m, Ar H). ^{13}C NMR ($CDCl_3$): 20.9 (Me), 31.8 (C_6), 52.2 (C_5), 74.3 (C_1), 81.3 (C_3), 90.2 (C_4), 112.2 (C_2), 121.6 (Ar CH), 123.9 (Ar CH), 126.3 (Ar CH), 132.4 (Ar C), 223.8 (CO(Mn)). Anal. Calcd: C, 53.51; H, 3.53. Found: C, 53.61; H, 3.74.

Substitution by Unsaturated Bonds. Typical Sonogashira Reaction Procedure: Preparation of Complex 9. Pd_2dba_3 (0.0178 g, 0.019 mmol) and $AsPh_3$ (0.021 g, 0.068 mmol) were added successively to complex **2c** (0.055 g, 0.195 mmol) in 6 mL of anhydrous degassed triethylamine. After 5 min at room temperature phenylacetylene (0.022 mL, 0.195 mmol) was introduced. The mixture was stirred for 4 h at 45 °C, poured into 20 mL of cold ice water, and extracted twice with diethyl ether (20 mL). The combined organic phases were washed with a saturated ammonium chloride solution (20 mL), dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The residue was then purified by flash chromatography on silica gel (petroleum ether/Et_2O, 90:10) to afford complex **9** in 79% yield. IR ($CHCl_3$): 1950, 2018 (CO(Mn)), 2208 (C≡C). ^{1}H NMR ($CDCl_3$): 2.46 (1H, d, J = 13 Hz, H_{6exo}), 2.92 (1H, dd, J = 6 and 13 Hz, H_{6endo}), 3.09 (1H, dd, J = 6 and 2.5 Hz, H_5), 5.23 (1H, d, J = 6 Hz, H_2), 5.79 (1H, dd, J = 2.5 and 6 Hz, H_3), 7.3 (5H, m, Ar H). ^{13}C NMR ($CDCl_3$): 32.0 (C_6), 36.3 (C_5), 47.3 (C_1), 54.5 (OMe), 67.9 (C_3), 86.1 (C(C≡C)), 90.2 (C(C≡C)), 97.1 (C_2), 123.2 (Ar CH), 128.1 (Ar CH), 128.3 (Ar CH), 130.6 (Ar C), 143.2 (C_4), 220.2 (CO(Mn)). Anal. Calcd: C, 62.08; H, 3.76. Found: C, 62.25; H, 4.02.

The same procedure was applied for the preparation of **10a**,**c** and **11. 10a** (40%). IR ($CHCl_3$): 1935, 2025 (CO(Mn)), 2147 (C≡C). ^{1}H NMR ($CDCl_3$): 0.15 (9H, s, Me), 2.23 (1H, d, J = 13 Hz, H_{6exo}), 2.77 (1H, dd, J = 13 and 6 Hz, H_{6endo}), 3.20 (1H, t, J = 6 Hz, H_5), 4.84 (1H, d, J = 5 and 6 Hz, H_4), 5.12 (1H, d, J = 5.5 Hz, H_2), 5.80 (1H, t, J = 5.5 Hz, H_3). ^{13}C NMR ($CDCl_3$): 0.10 (Me), 29.8 (C_6), 51.6 (C_5), 66.0 (C_1), 78.9 (C_3), 90.8 (C(C≡C)), 97.4 (C_2), 100.6 (C_4), 106.7 (C(C≡C)), 222.1 (CO(Mn)). Anal. Calcd: C, 53.50; H, 4.81. Found: C, 53.28; H, 4.67.

10c (78%). IR ($CHCl_3$): 1938, 2025 (CO(Mn)), 2150 (C≡C). ^{1}H NMR ($CDCl_3$): 0.12 (9H, s, Me), 2.33 (1H, d, J = 13 Hz, H_{6exo}), 2.83 (1H, dd, J = 13 and 6 Hz, H_{6endo}), 2.97 (1H, d, J = 6 Hz, H_5), 3.76 (3H, s, OMe), 5.13 (1H, d, J = 5 Hz, H_2), 5.70 (1H, d, J = 5 Hz, H_3). ^{13}C NMR ($CDCl_3$): 0.13 (Me), 31.6 (C_6), 36.2 (C_5), 46.1 (C_1), 54.4 (OMe), 68.1 (C_3), 90.9 (C(C≡C)), 97.6 (C_2), 106.1 (C(C≡C)), 143.3 (C_4), 221.2 (CO(Mn)). Anal. Calcd: C, 52.32; H, 4.98. Found: C, 52.49; H, 4.74.

11 (95%). ^{1}H NMR ($CDCl_3$): 1.87 (3H, s, Me), 2.39 (1H, d, J = 13 Hz, H_{6exo}), 2.91 (1H, dd, J = 13 and 6 Hz, H_{6endo}), 3.11 (1H, d, J = 6 Hz, H_1), 5.16 (1H, d, J = 5 Hz, H_4), 5.74 (1H, d, J = 5 Hz, H_3), 7.29 (3H, m, Ar H), 7.38 (2H, m, Ar H). ^{13}C NMR ($CDCl_3$): 21.3 (Me), 29.9 (C_6), 45.3 (C_5), 51.7 (C_1), 78.9 (C_3), 84.8 (C(C≡C)), 89.6 (C(C≡C)), 97.8 (C_4), 111.3 (Ar C), 122.2 (C_2), 127.0 (Ar CH), 127.2 (Ar CH), 130.5 (Ar CH), 221.3 (CO(Mn)). Anal. Calcd: C, 65.07; H, 3.94. Found: C, 65.25; H, 4.21.

Typical Stille Reaction Procedure: Preparation of Complex 8. Pd_2dba_3 (0.014 g, 0.016 mmol) and $AsPh_3$ (0.017 g, 0.056 mmol) were added successively to complex **2a** (0.040 g, 0.16 mmol) in 5 mL of anhydrous degassed DMF. After 5 min at room temperature tributylstannylethynylbenzene (0.056 mL, 0.16 mmol) was introduced. The mixture was stirred half an hour, cold ice water (20 mL) was then added, and the reaction mixture was extracted twice with pentane (20 mL). The combined organic phases were washed with water (3 × 20 mL) and a saturated ammonium chloride solution (20 mL), dried over magnesium sulfate, filtered, and evaporated under

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reduced pressure. The residue was then purified by flash chromatography on silica gel (petroleum ether/Et_2O, 90:10) to afford complex **8** in 91% yield. IR ($CHCl_3$): 1947, 2022 (CO(Mn)), 2203 (C≡C). ^{1}H NMR ($CDCl_3$): 2.41 (1H, d, J = 13 Hz, H_{6exo}), 2.94 (1H, dd, J = 13 and 6 Hz, H_{6endo}), 3.23 (1H, d, J = 6 Hz, H_5), 4.93 (1H, dd, J = 5 and 6 Hz, H_4), 5.22 (1H, d, J = 5 Hz, H_2), 5.89 (1H, t, J = 5 Hz, H_3), 7.30−7.42 (5H, m, Ar H). ^{13}C NMR ($CDCl_3$): 29.7 (C_6), 52.5 (C_5), 78.8 (C_1), 87.3 (C_3), 95.0 (C(C≡C)), 97.3 (C_2), 100.2 (C_4), 103.2 (C(C≡C)), 128.2 (Ar CH), 128.4 (Ar CH), 131.7 (Ar CH), 134.8 (Ar C), 219.6 (CO(Mn)). Anal. Calcd: C, 64.17; H, 3.48. Found: C, 64.52; H, 3.37.

Preparation of complexes **12*Z*-*E*** and **13*Z*-*E*** was achieved with the same protocol substituting tributylstannylethynylbenzene by tributylstyrylstannane. **12*Z*** (27%). IR ($CHCl_3$): 1935, 2015 (CO(Mn)), 1619 (C═C). ^{1}H NMR ($CDCl_3$): 2.12 (1H, d, J = 13 Hz, H_{6exo}), 2.37 (1H, dd, J = 6 and 13 Hz, H_{6endo}), 2.80 (1H, dd, J = 2.5 and 6 Hz, H_5), 3.41 (3H, s, OMe), 4.84 (1H, d, J = 5.5 Hz, H_2), 5.48 (1H, d, J = 11 Hz, H(C═C)), 5.66 (1H, dd, J = 5.5 and 2.5 Hz, H_3), 6.42 (1H, d, J = 11 Hz, H(C═C)), 7.30 (5H, m, Ar H). ^{13}C NMR ($CDCl_3$): 31.3 (C_6), 36.7 (C_5), 68.5 (C_1), 55.5 (OMe), 67.5 (C_3), 86.1 (C(C═C)), 90.2 (C(C═C)), 95.9 (C_2), 128.1 (Ar CH), 128.9 (Ar CH), 133.1 (Ar CH), 139.9 (Ar C), 144.3 (C_4), 222.9 (CO(Mn)). Anal. Calcd: C, 61.73; H, 4.32. Found: C, 61.66; H, 4.40. **12*E*** (36%). IR ($CHCl_3$): 1933, 2011 (CO(Mn)), 1622 (C═C). ^{1}H NMR ($CDCl_3$): 2.36 (1H, d, J = 13 Hz, H_{6exo}), 3.09 (1H, dd, J = 13 and 6 Hz, H_{6endo}), 3.24 (1H, d, J = 6 Hz, H_5), 3.52 (3H, s, OMe), 4.87 (1H, d, J = 5 Hz, H_2), 5.74 (1H, d, J = 5 Hz, H_3), 6.38 (1H, d, J = 16 Hz, H(C═C)), 6.12 (1H, d, J = 16 Hz, H(C═C)), 7.21−7.38 (5H, m, Ar H). ^{13}C NMR ($CDCl_3$): 26.0 (C_6), 35.4 (C_5), 53.4 (OMe), 64.9 (C_1), 67.6 (C_3), 97.5 (C_2), 125.3 (Ar CH), 126.2 (Ar CH or CH(C═C)), 126.5 (Ar CH or CH(C═C)), 127.6 (Ar CH), 129.3 (CH(C═C)), 135.9 (Ar C), 142.5 (C_4), 222.2 (CO(Mn)). Anal. Calcd: C, 61.73; H, 4.32. Found: C, 61.87; H, 4.37.

13*Z*-*E* (global yield 29%). IR ($CHCl_3$): 1938, 2020 (CO(Mn)), 2210 (C≡C). ^{1}H NMR ($CDCl_3$): 2.10 (1H, d, J = 13 Hz, $H_{6exo(Z)}$), 2.18 (1H, d, J = 13 Hz, $H_{6exo(E)}$), 2.66 (1H, dd, J = 6 and 13 Hz, $H_{6endo(E)}$), 2.73 (1H, dd, J = 6 and 13 Hz, $H_{6endo(Z)}$), 2.93 (1H, d, J = 6 Hz, $H_{1(E)}$), 3.25 (2H, m, $H_{5(Z)}$, $H_{5(E)}$), 3.28 (1H, d, J = 5.5 Hz, $H_{1(Z)}$), 4.75 (1H, t, J = 6 Hz, $H_{4(E)}$), 4.91 (1H, t, J = 6 Hz, $H_{4(Z)}$), 5.47 (1H, t, J = 6 Hz, $H_{3(E)}$), 6.10 (1H, d, J = 6 Hz, $H_{3(Z)}$), 6.44 (1H, d, J = 16 Hz, H(C═C)$_{(E)}$), 6.84 (1H, d, J = 16 Hz, H(C═C)$_{(E)}$), 7.92 (1H, d, J = 5 Hz, H(C═C)$_{(Z)}$), 7.29−7.34 (11H, m, Ar H and H(C═C)$_{(Z)}$). ^{13}C NMR ($CDCl_3$): 25.3 and 25.9 ($C_{6(Z)}$ and $C_{6(E)}$), 46.0 and 51.2 ($C_{5(Z)}$ and $C_{5(E)}$), 51.3 and 51.7 ($C_{1(Z)}$ and $C_{1(E)}$), 79.2 and 83.4 ($C_{3(Z)}$ and $C_{3(E)}$), 96.9 and 97.8 ($C_{2(Z)}$ and $C_{2(E)}$), 111.6 and 112.3 ($C_{4(Z)}$ and $C_{4(E)}$), 127.0 and 127.5 (C(C═C)$_{(Z)}$ and C(C═C)$_{(E)}$), 128.6 and 128.8 (Ar H$_{(Z)}$ and Ar H$_{(E)}$), 128.9 and 129.0 (Ar H$_{(Z)}$ and Ar H$_{(E)}$), 129.1 and 129.3 (Ar H$_{(Z)}$ and Ar H$_{(E)}$), 131.1 (C(C═C)$_{(Z)}$ or C(C═C)$_{(E)}$), 133.8 and 133.9 (Ar H$_{(Z)}$ and Ar H$_{(E)}$), 134.6 (C(C═C)$_{(Z)}$ or C(C═C)$_{(E)}$), 223.0 and 223.1 (CO(Mn)$_{(Z)}$ and CO(Mn)$_{(E)}$). Anal. Calcd: C, 63.76; H, 4.09. Found: C, 63.52; H, 3.84.

Typical Heck Reaction Procedure: Synthesis of Complex 14. Pd_2dba_3 (0.037 g, 0.04 mmol), $AsPh_3$ (0.043 g, 0.14 mmol), and potassium carbonate (0.166 g, 1.20 mmol) were added successively to complex **2c** (0.114 g, 0.40 mmol) in 5 mL of anhydrous degassed DMF. After 10 min at room temperature, phenylacrylate (0.066 mL, 0.40 mmol) was introduced. The mixture was stirring 1.5 h, cold ice water (15 mL) was then added, and the reaction mixture was extracted twice with diethyl ether (20 mL). The combined organic phases were washed with a saturated ammonium chloride solution (20 mL), dried over magnesium sulfate, filtered, and evaporated under nitrogen flush. The residue was then purified by flash chromatography on silica gel (petroleum ether/Et_2O, 80:20) to deliver complex **14** in 18% yield. IR ($CHCl_3$): 1948, 2020 (CO(Mn)), 1718 (CO), 1627 (C═C). ^{1}H NMR ($CDCl_3$): 2.26 (1H, d, J = 13 Hz, H_{6exo}), 3.00 (1H, dd, J = 6 and 13 Hz, H_{6endo}), 3.19 (1H, dd, J = 6 and 2.5 Hz, H_5), 3.51 (3H, s, OMe), 5.18 (1H, d, J = 6 Hz, H_2), 5.85 (1H, dd, J = 2.5 and 6 Hz, H_3), 5.90 (1H, d, J = 15 Hz, H(C═C)), 6.90 (1H, d, J = 15 Hz, H(C═C)), 7.12 (2H, d, J = 7.5 Hz, Ar H), 7.23 (1H, t, J = 7.5 Hz, Ar H), 7.38 (2H, t, J = 7.5 Hz, Ar H). ^{13}C NMR ($CDCl_3$): 26.7 (C_6), 37.3 (C_5), 54.7 (OMe), 59.2 (C_1), 69.4 (C_3), 98.3 (C_2), 114.0 (C(C═C)), 121.7 (Ar CH), 125.8 (Ar CH), 129.5 (Ar CH), 144.4 (C_4), 150.4 (C(C═C)), 150.8 (Ar C), 165.2 (CO), 220.1 (CO(Mn)). Anal. Calcd: C, 57.89; H, 3.83. Found: C, 57.69; H, 4.06.

15 (13%). IR ($CHCl_3$): 1937, 2018 (CO(Mn)), 1722 (CO), 1623 (C═C). ^{1}H NMR ($CDCl_3$): 1.28 (3H, t, J = 7 Hz, Me), 2.24 (1H, d, J = 13 Hz, H_{6exo}), 2.91 (1H, dd, J = 6 and 13 Hz, H_{6endo}), 3.12 (1H, d, J = 6 Hz, H_5), 3.49 (3H, s, OMe), 4.18 (2H, q, J = 7 Hz, CH_2), 5.10 (1H, d, J = 6 Hz, H_2), 5.63 (1H, d, J = 15.5 Hz, H(C═C)), 5.82 (1H, d, J = 6 Hz, H_3), 6.73 (1H, d, J = 15.5 Hz, H(C═C)). ^{13}C NMR ($CDCl_3$): 14.4 (Me), 26.7 (C_6), 37.1 (C_5), 54.6 (OMe), 60.1 (C_1), 60.4 (*C*H$_2$), 68.8 (C_3), 97.7 (C_2), 115.4 (C(C═C)), 144.3 (C_4), 148.1 (C(C═C)), 166.8 (CO), 221.5 (CO(Mn)). Anal. Calcd: C, 52.04; H, 4.37. Found: C, 52.19; H, 4.45.

Typical Carbonylation Procedure: Preparation of 16b. Pd_2dba_3 (0.023 g, 0.025 mmol) and $AsPh_3$ (0.027 g, 0.088 mmol) were added successively to complex **2b** (0.067 g, 0.25 mmol) in 10 mL of anhydrous THF. Carbon monoxide was pulled through the reaction mixture, and tributylstannylthiophene (0.033 mL, 0.25 mmol) was introduced. The solution was stirred for 2.5 h at reflux, cold ice water (15 mL) was then added, and the reaction mixture was extracted twice with diethyl ether (20 mL). The combined organic phases were washed with water (20 mL), dried over magnesium sulfate, filtered, and evaporated under nitrogen flush. The residue was then purified by flash chromatography on silica gel (petroleum ether/Et_2O, 80:20) to deliver complex **16b** in 90% yield. IR ($CHCl_3$): 1958, 2027 (CO(Mn)), 1606 (CO). ^{1}H NMR ($CDCl_3$): 1.96 (3H, s, Me), 2.33 (1H, d, J = 13 Hz, H_{6exo}), 3.50 (1H, dd, J = 13 and 6 Hz, H_{6endo}), 3.32 (1H, d, J = 6 Hz, H_5), 6.01 (2H, m, H_2, H_3), 7.41 (3H, m, Ar H). ^{13}C NMR ($CDCl_3$): 22.2 (Me), 27.2 (C_6), 53.4 (C_5), 55.8 (C_1), 84.1 (C_3), 101.3 (C_2), 121.8 (C_4), 126.5 (Ar CH), 129.0 (Ar CH), 132.0 (Ar CH), 134.1 (Ar C), 189.4 (CO), 225.5 (CO(Mn)). Anal. Calcd: C, 52.63; H, 3.21. Found: C, 52.41; H, 3.00.

16c (90%). IR ($CHCl_3$): 1957, 2027 (CO(Mn)), 1606 (CO). ^{1}H NMR ($CDCl_3$): 2.38 (1H, d, J = 13 Hz, H_{6exo}), 3.19 (1H, dd, J = 13 and 5 Hz, H_{6endo}), 3.43 (1H, d, J = 5 Hz, H_5), 3.48 (3H, s, OMe), 6.05 (1H, d, J = 6 Hz, H_2), 6.13 (1H, d, J = 6 Hz, H_3), 7.06 (1H, dd, J = 4 and 5 Hz, Ar H), 7.48 (1H, dd, J = 4 and 1 Hz, Ar H), 7.55 (1H, dd, J = 5 and 1 Hz, Ar H). ^{13}C NMR ($CDCl_3$): 26.9 (C_6), 31.1 (C_5), 38.1 (C_1), 54.8 (OMe), 72.6 (C_3), 100.4 (C_2), 127.6 (Ar CH), 131.0 (Ar CH), 132.2 (Ar CH), 142.6 (Ar C), 144.5 (C_4), 188.9 (CO), 225.5 (CO(Mn)). Anal. Calcd: C, 50.29; H, 3.26. Found: C, 50.54; H, 3.51.

16f (73%). IR ($CHCl_3$): 1963, 2026 (CO(Mn)), 1610 (CO). ^{1}H NMR ($CDCl_3$): 3.52 (3H, s, OMe), 3.80 (1H, dd, J = 2.5 and 6.5 Hz, H_5), 4.80 (1H, d, J = 6.5 Hz, H_{6endo}), 5.88 (1H, d, J = 6.5 Hz, H_2), 6.05 (1H, dd, J = 2.5 and 6.5 Hz, H_3), 6.92 (2H, d, J = 7.5 Hz, Ar H), 7.01 (1H, dd, J = 5 and 4 Hz, Ar H), 7.15 (3H, m, Ar H), 7.43 (1H, dd, J = 4 and 1 Hz, Ar H), 7.48 (1H, dd, J = 5 and 1 Hz, Ar H). ^{13}C NMR ($CDCl_3$): 40.6 (C_5), 45.1 (C_6), 55.0 (OMe), 61.2 (C_1), 72.4 (C_3), 97.9 (C_2), 125.6 (Ar CH), 127.0 (Ar CH), 127.6 (Ar CH), 128.7 (Ar CH), 130.7 (Ar CH), 132.1 (Ar CH), 142.1 (Ar C), 144.0 (Ar C), 146.2 (C_4), 188.4 (CO), 220.0 (CO(Mn)). Anal. Calcd: C, 58.08; H, 3.48. Found: C, 57.92; H, 3.22.

17b (56%). IR ($CHCl_3$): 1962, 2030 (CO(Mn)), 1656 (CO). ^{1}H NMR ($CDCl_3$): 0.90 (3H, t, J = 7 Hz, Me), 1.36 (4H, m, CH_2), 1.61 (2H, t, J = 7 Hz, CH_2), 1.92 (3H, s, Me), 2.35 (1H, d, J = 13 Hz, H_{6exo}), 3.14 (1H, dd, J = 6 and 13 Hz, H_{6endo}), 3.28 (1H, d, J = 6 Hz, H_5), 5.70 (1H, d, J = 6 Hz, H_2), 5.92 (1H, d, J = 6 Hz, H_3). ^{13}C NMR ($CDCl_3$): 13.8 (Me), 22.1 (*C*H$_2$), 22.4 (*C*H$_2$), 26.2 (Me), 27.4 (*C*H$_2$), 27.8 (C_6), 53.1 (C_1), 56.6 (C_5), 83.4 (C_3), 98.6 (C_2), 128.4 (C_4), 203.5 (CO), 221.5 (CO(Mn)). *M*/*z*: 316.11.

17c (45%). IR ($CHCl_3$): 1961, 2030 (CO(Mn)), 1656 (CO). ^{1}H NMR ($CDCl_3$): 0.89 (3H, t, J = 7 Hz, CH_3), 1.25 (2H, q, J

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= 7 Hz, CH_2), 1.32 (2H, q, J = 7 Hz, CH_2), 1.55 (2H, t, J = 7 Hz, CH_2), 1.96 (1H, d, J = 13 Hz, H_{6exo}), 2.28 (1H, dd, J = 7 and 13 Hz, H_{6endo}), 3.29 (1H, d, J = 7 Hz, H_5), 3.46 (3H, s, OMe), 5.79 (1H, d, J = 6 Hz, H_2), 5.95 (1H, d, J = 6 Hz, H_3). ^{13}C NMR ($CDCl_3$): 14.0 (Me), 22.4 (*C*H$_2$), 25.1 (*C*H$_2$), 26.4 (C_6), 26.5 (*C*H$_2$), 35.9 (C_5), 38.6 (C_1), 54.8 (OMe), 72.2 (C_3), 97.7 (C_2), 144.7 (C_4), 203.0 (CO), 220.4 (CO(Mn)). Anal. Calcd: C, 54.27; H, 5.16. Found: C, 54.54; H, 5.53.

18 (69%). IR ($CHCl_3$): 1960, 2023 (CO(Mn)), 1614 (CO). ^{1}H NMR ($CDCl_3$): 2.10 (3H, s, Me), 3.53 (3H, s, OMe), 3.72 (1H, dd, J = 2 and 5 Hz, H_5), 4.50 (1H, d, J = 6.5 Hz, H_{6endo}), 5.86 (2H, m, H_3, H_2), 6.92 (1H, d, J = 6.5 Hz, Ar H), 7.17 (3H, m, Ar H). ^{13}C NMR ($CDCl_3$): 23.5 (Me), 38.5 (C_5), 44.1 (C_6), 53.9 (OMe), 61.5 (C_1), 70.8 (C_3), 95.4 (C_2), 124.7 (Ar CH), 125.9 (Ar CH), 127.3 (Ar CH), 143.0 (Ar C), 144.8 (C_4), 198.8 (CO), 220.2 (CO(Mn)). Anal. Calcd: C, 59.02; H, 4.13. Found: C, 59.09; H, 4.15.

16d (26%). IR ($CHCl_3$): 1961, 2027 (CO(Mn)), 1609 (CO). ^{1}H NMR ($CDCl_3$): 2.08 (3H, s, Me), 2.38 (1H, d, J = 12.5 Hz, H_{6exo}), 2.73 (1H, td, J = 5 and 2 Hz, H_5), 3.19 (1H, dd, J = 5 and 12.5 Hz, H_{6endo}), 4.75 (1H, t, J = 5 Hz, H_4), 6.05 (1H, dd, J = 5 and 2 Hz, H_3), 7.34 (1H, t, J = 4 Hz, Ar H), 7.45 (1H, d, J = 4 Hz, Ar H), 7.58 (1H, d, J = 4 Hz, Ar H). ^{13}C NMR ($CDCl_3$): 21.7 (Me), 28.6 (C_6), 50.5 (C_5), 68.3 (C_1), 78.9 (C_2), 82.4 (C_3), 100.8 (C_4), 126.8 (Ar CH), 130.4 (Ar CH), 132.3 (Ar CH), 133.7 (Ar C), 188.7 (CO), 225.8 (CO(Mn)). Anal. Calcd: C, 52.63; H, 3.21. Found: C, 52.41; H, 3.08.

19 (70%). IR ($CHCl_3$): 1959, 2024 (CO(Mn)), 1602 (CO). ^{1}H NMR ($CDCl_3$): 2.06 (1H, d, J = 13 Hz, H_{6exo}), 2.63 (1H, dd, J = 6 and 13 Hz, H_{6endo}), 2.85 (1H, d, J = 6 Hz, H_1), 2.91 (1H, t, J = 6 Hz, H_5), 4.82 (1H, d, J = 6 Hz, H_4), 5.90 (1H, d, J = 6 Hz, H_3), 7.34 (1H, m, Ar H), 7.55 (1H, m, Ar H), 7.73 (1H, m, Ar H). ^{13}C NMR ($CDCl_3$): 23.2 (C_6), 29.9 (Me), 49.9 (C_5), 50.4 (C_1), 78.8 (C_3), 97.0 (C_4), 115.3 (C_2), 127.4 (Ar CH), 127.6 (Ar CH), 132.7 (Ar CH), 138.6 (Ar C), 166.7 (CO), 222.2 (CO(Mn)). Anal. Calcd: C, 51.23; H, 2.76. Found: C, 51.31; H, 2.72.

Following the same procedure by using phenol, methanol, morpholine, or *p*-(tolyl)SH as nucleophile allows the preparation of complexes **20**, **21**, **22**, and **23**, respectively.

20 (71%). IR ($CHCl_3$): 1958, 2029 (CO(Mn)), 1716 (CO). ^{1}H NMR ($CDCl_3$): 2.12 (1H, d, J = 12 Hz, H_{6exo}), 3.25 (1H, dd, J = 4 and 12 Hz, H_{6endo}), 3.29 (1H, d, J = 4 Hz, H_5), 3.46 (3H, s, OMe), 6.04 (1H, d, J = 6 Hz, H_2), 6.12 (1H, d, J = 6 Hz, H_3), 7.07 (2H, d, J = 8 Hz, Ar H), 7.22 (1H, t, J = 8 Hz, Ar H), 7.38 (2H, t, J = 8 Hz, Ar H). ^{13}C NMR ($CDCl_3$): 24.6 (C_6), 37.7 (C_5), 42.9 (C_1), 53.7 (OMe), 72.0 (C_3), 97.9 (C_2), 120.5 (Ar CH), 124.6 (Ar CH), 128.4 (Ar CH), 143.3 (Ar C), 149.8 (C_4), 168.2 (CO), 222.7 (CO(Mn)). Anal. Calcd: C, 55.45; H, 3.56. Found: C, 55.15; H, 3.61.

21. ^{1}H NMR ($CDCl_3$): 2.05 (1H, d, J = 12 Hz, H_{6exo}), 3.15 (2H, m, H_{6endo}, H_5), 3.40 (3H, s, OMe), 3.67 (3H, s, (CO)OMe), 5.90 (2H, m, H_2, H_3). ^{13}C NMR ($CDCl_3$): 25.8 (C_6), 38.8 (C_5), 45.3 (C_1), 52.0 (CO_2Me), 54.0 (OMe), 72.3 (C_3), 98.6 (C_2), 143.3 (C_4), 188.9 (CO), 222.6 (CO(Mn)).

22 (48%). IR ($CHCl_3$): 1942, 2026 (CO(Mn)), 1612 (CO). ^{1}H NMR ($CDCl_3$): 2.33 (1H, d, J = 11.5 Hz, H_{6exo}), 2.98 (1H, dd, J = 1.5 and 6 Hz, H_5), 3.35 (1H, dd, J = 11.5 and 6 Hz, H_{6endo}), 3.44 (7H, m, OMe, NCH_2), 3.60 (4H, t, J = 4.5 Hz, OCH_2), 5.42 (1H, d, J = 6 Hz, H_2), 5.78 (1H, dd, J = 6 and 1.5 Hz, H_3). ^{13}C NMR ($CDCl_3$): 29.8 (C_6), 34.9 (C_5), 45.6 (N*C*H$_2$), 54.6 (OMe), 58.7 (C_1), 66.9 (O*C*H$_2$), 68.0 (C_3), 98.6 (C_2), 143.7 (C_4), 170.7 (CO), 222.9 (CO(Mn)). Anal. Calcd: C, 49.87; H, 4.46; N, 3.87. Found: C, 49.69; H, 4.47; N, 3.70.

23 (22%). IR ($CHCl_3$): 1941, 2033 (CO(Mn)), 1719 (CO). ^{1}H NMR ($CDCl_3$): 2.17 (1H, d, J = 11 Hz, H_{6exo}), 2.35 (3H, s, Me), 3.23 (2H, m, H_5, H_{6endo}), 3.47 (3H, s, OMe), 5.99 (2H, m, H_3, H_2), 7.19 (2H, d, J = 8 Hz, Ar H), 7.28 (2H, d, J = 8 Hz, Ar H). ^{13}C NMR ($CDCl_3$): 21.4 (Me), 30.1 (C_6), 38.9 (C_5), 53.5 (OMe), 65.6 (C_1), 72.2 (C_3), 97.1 (C_2), 123.8 (C_8), 130.0 (Ar CH), 135.0 (Ar CH), 139.6 (Ar CH), 144.5 (C_4), 192.4 (CO), 224.8 (CO(Mn)). Anal. Calcd: C, 54.28; H, 3.80. Found: C, 53.90; H, 4.01.

Synthesis of Yne/ene-one: Preparation of 24. Pd_2dba_3 (0.027 g, 0.029 mmol) and $AsPh_3$ (0.031 g, 0.10 mmol) were added successively to complex **2c** (0.082 g, 0.29 mmol) in 8 mL of anhydrous triethylamine. Carbon monoxide was pulled through the reaction mixture, and trimethylsilylacetylene (0.045 mL, 0.32 mmol) was introduced. The solution was stirred for 7 h at 40 °C, cold ice water (15 mL) was then added, and the reaction mixture was extracted twice with diethyl ether (20 mL). The combined organic phases were washed with a saturated ammonium chloride solution (20 mL), dried over magnesium sulfate, filtered, and evaporated under nitrogen flush. The residue was then purified by flash chromatography on silica gel (petroleum ether/Et_2O, 90:10) to deliver complex **24** in 74% yield. IR ($CHCl_3$): 1960, 2030 (CO(Mn)), 2153 (C≡C), 1721 (CO). ^{1}H NMR ($CDCl_3$): 0.21 (9H, s, Me), 1.94 (1H, d, J = 12 Hz, H_{6exo}), 3.10 (1H, dd, J = 6 and 12 Hz, H_{6endo}), 3.16 (1H, d, J = 6 Hz, H_5), 3.47 (3H, s, OMe), 5.90 (1H, m, H_2), 6.02 (1H, m, H_3). ^{13}C NMR ($CDCl_3$): 2.35 (Me), 24.9 (C_6), 31.2 (C_5), 55.1 (OMe), 57.5 (C_1), 73.9 (C_3), 99.7 and 100.8 (C(C≡C)), 101.0 (C_2), 145.7 (C_4), 180.6 (CO), 227.8 (CO(Mn)). Anal. Calcd: C, 51.61; H, 4.60. Found: C, 51.93; H, 4.46.

Performing the same reaction by substituting tributylstyrylstannane with trimethylsilylacetylene and DMF with Et_3N led to complexes **25*Z*** (27%) and **25*E*** (28%). **25*Z*.** IR ($CHCl_3$): 1948, 2024 (CO(Mn)), 1716 (CO), 1624 (C=C). ^{1}H NMR ($CDCl_3$): 2.07 (1H, d, J = 13 Hz, H_{6exo}), 3.24 (1H, dd, J = 6 and 2 Hz, H_5), 3.34 (1H, dd, J = 6 and 13 Hz, H_{6endo}), 3.49 (3H, s, OMe), 5.93 (1H, d, J = 6.5 Hz, H_2), 6.05 (1H, dd, J = 6.5 and 2 Hz, H_3), 6.83 (1H, d, J = 16 Hz, H(C=C)), 7.35 (3H, m, Ar H), 7.52 (2H, t, J = 5 Hz, Ar H), 7.66 (1H, d, J = 16 Hz, H(C=C)). ^{13}C NMR ($CDCl_3$): 27.0 (C_6), 38.8 (C_5), 54.6 (OMe), 55.7 (C_1), 72.7 (C_3), 98.0 (C_2), 118.7 (CH(C=C)), 128.3 (Ar CH), 129.0 (Ar CH), 130.3 (Ar CH), 135.0 (Ar CH), 143.0 (CH(C=C)), 144.7 (C_4), 191.8 (CO), 225.6 (CO(Mn)). Anal. Calcd: C, 60.33; H, 4.00. Found: C, 60.18; H, 3.95. **25*E*** (28%). IR ($CHCl_3$): 1952, 2026 (CO(Mn)), 1718 (CO), 1622 (C=C). ^{1}H NMR ($CDCl_3$): 1.88 (1H, d, J = 12 Hz, H_{6exo}), 3.22 (2H, m, H_5, H_{6endo}), 3.43 (3H, s, OMe), 5.40 (1H, d, J = 5 Hz, H_2), 5.67 (1H, d, J = 8 Hz, H(C=C)), 5.77 (1H, d, J = 8 Hz, H(C=C)), 5.88 (1H, d, J = 5 Hz, H_3), 7.31 (5H, m, Ar H). ^{13}C NMR ($CDCl_3$): 25.0 (C_6), 38.4 (C_5), 54.2 (C_1), 54.7 (OMe), 72.4 (C_3), 99.6 (C_2), 116.7 (CH(C=C)), 125.9 (Ar CH), 128.6 (Ar CH), 129.0 (Ar CH), 135.8 (Ar C), 144.7 (C_4), 147.7 (CH(C=C)), 200.4 (CO), 221.8 (CO(Mn)). Anal. Calcd: C, 60.33; H, 4.00. Found: C, 60.27; H, 3.92.

Pd-Catalyzed Nucleophilic Substitution. Pd_2dba_3 (0.020 g, 0.018 mmol), $AsPh_3$ (0.021 g, 0.070 mmol), potassium cyanide (0.052 g, 0.80 mmol), and crown ether 18c6 (0.068 g, 0.26 mmol) were added to a solution of complex **2c** (0.057 g, 0.20 mmol) in degassed DMF (5 mL). After stirring 7 h at reflux, water was added (20 mL) and the reaction mixture was extracted twice with ethyl acetate (20 mL). The combined organic phases were washed with water (4 × 20 mL), dried over magnesium sulfate, filtered, and evaporated under nitrogen flush. Complex **26** could not be purified. ^{1}H NMR ($CDCl_3$): 2.80−2.97 (3H, m, H_{6exo}, H_{6endo}, H_5), 3.53 (3H, s, OMe), 5.07 (1H, d, J = 5.5 Hz, H_2), 6.06 (1H, d, J = 5.5 Hz, H_3). ^{13}C NMR ($CDCl_3$): 29.8 (C_6), 35.0 (C_5), 56.0 (OMe), 75.9 (C_3), 95.0 (C_1), 118.5 (C_2), 121.5 (CN), 149.5 (C_4), 222.7 (CO(Mn)).

Typical Substitution Procedure: Preparation of 27a. Pd_2dba_3 (0.019 g, 0.021 mmol), $AsPh_3$ (0.022 g, 0.07 mmol), and cesium carbonate (0.082 g, 0.25 mmol) were added successively to complex **2a** (0.053 g, 0.21 mmol) in 8 mL of anhydrous THF. After stirring 10 min, morpholine (0.020 mL, 0.20 mmol) was introduced. After refluxing for 5.5 h, cold ice water (15 mL) was added and the reaction mixture was extracted twice with diethyl ether (20 mL). The combined organic phases were washed with a saturated ammonium chloride solution (20 mL), dried over magnesium sulfate, filtered, and evaporated under nitrogen flush. The residue was then purified by flash chromatography on silica gel (petroleum ether/Et_2O, 70:30) to deliver complex **27a** in 84% yield. IR

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($CHCl_3$): 1950, 1995 (CO(Mn)). ^1H NMR ($CDCl_3$): 2.47 (1H, d, $J = 14$ Hz, H_{6exo}), 2.78 (1H, td, $J = 6$ and 1.5 Hz, H_5), 2.95 (4H, t, $J = 5$ Hz, NCH_2), 3.25 (1H, dd, $J = 6$ and 14 Hz, H_{6endo}), 3.49 (1H, d, $J = 6$ Hz, H_2), 3.70 (4H, t, $J = 5$ Hz, OCH_2), 4.97 (1H, t, $J = 6$ Hz, H_4), 5.54 (1H, dd, $J = 6$ and 1.5 Hz, H_3). ^{13}C NMR ($CDCl_3$): 27.0 (C_6), 42.8 (C_5), 47.0 (NCH_2), 65.9 (OCH_2), 68.9 (C_1), 73.8 (C_3), 91.0 (C_2), 120.9 (C_4), 225.6 (CO(Mn)). Anal. Calcd: C, 54.50; H, 4.65; N, 4.62. Found: C, 54.32; H, 4.79; N, 4.43.

27b (76%). IR ($CHCl_3$): 1910, 1995 (CO(Mn)). ^1H NMR ($CDCl_3$): 1.91 (3H, s, Me), 2.51 (1H, d, $J = 14$ Hz, H_{6exo}), 2.77 (1H, dd, $J = 5.5$ and 2 Hz, H_5), 2.90 (4H, t, $J = 6$ Hz, NCH_2), 3.19 (1H, dd, $J = 14$ and 5.5 Hz, H_{6endo}), 3.48 (1H, d, $J = 6$ Hz, H_2), 3.70 (4H, t, $J = 6$ Hz, OCH_2), 5.40 (1H, dd, $J = 6$ and 2 Hz, H_3). ^{13}C NMR ($CDCl_3$): 22.1 (Me), 28.3 (C_6), 43.3 (C_5), 47.2 (NCH_2), 66.0 (OCH_2), 67.7 (C_1), 73.8 (C_3), 106.6 (C_2), 119.2 (C_4), 225.6 (CO(Mn)). Anal. Calcd: C, 53.01; H, 5.08; N, 4.42. Found: C, 53.34; H, 5.20; N, 4.11.

27c (90%). IR ($CHCl_3$): 1910, 1996 (CO(Mn)). ^1H NMR ($CDCl_3$): 2.58 (1H, d, $J = 14$ Hz, H_{6exo}), 2.86 (4H, t, $J = 5.5$ Hz, NCH_2), 2.93 (1H, dd, $J = 6$ and 2.5 Hz, H_5), 3.25 (1H, ddd, $J = 6$, 14 and 2.5 Hz, H_{6endo}), 3.47 (1H, dd, $J = 6$ and 2.5 Hz, H_2), 3.57 (3H, s, OMe), 3.69 (4H, t, $J = 5.5$ Hz, OCH_2), 5.33 (1H, dd, $J = 6$ and 2.5 Hz, H_3). ^{13}C NMR ($CDCl_3$): 29.2 (C_6), 35.2 (C_5), 47.6 (NCH_2), 54.3 (OMe), 58.1 (C_3), 64.5 (C_1), 66.0 (OCH_2), 118.4 (C_2), 140.6 (C_4), 225.0 (CO(Mn)). Anal. Calcd: C, 50.46; H, 4.84; N, 4.20. Found: C, 50.71; H, 4.95; N, 3.96.

27f (55%). IR ($CHCl_3$): 1910, 1994 (CO(Mn)). ^1H NMR ($CDCl_3$): 2.88 (4H, t, $J = 4.5$ Hz, NCH_2), 3.43 (1H, dd, $J = 6$ and 2.5 Hz, H_5), 3.60 (3H, s, OMe), 3.64 (4H, t, $J = 4.5$ Hz, OCH_2), 3.83 (1H, d, $J = 6$ Hz, H_2), 4.46 (1H, d, $J = 6$ Hz, H_{6endo}), 5.28 (1H, dd, $J = 6$ and 2.5 Hz, H_3), 6.97 (2H, t, $J = 6.5$ Hz, Ar H), 7.16 (3H, m, Ar H). ^{13}C NMR ($CDCl_3$): 43.0 (C_6), 44.1 (C_5), 47.6 (NCH_2), 54.3 (OMe), 58.3 (C_1), 65.2 (C_3), 65.9 (OCH_2), 120.1 (C_2), 125.8 (Ar CH), 127.0 (Ar CH), 128.8 (Ar CH), 139.3 (Ar C), 144.9 (C_4), 225.6 (CO(Mn)). Anal. Calcd: C, 58.69; H, 4.92; N, 3.42. Found: C, 58.88; H, 4.87; N, 3.22.

28 (84%). IR ($CHCl_3$): 1911, 1995 (CO(Mn)). ^1H NMR ($CDCl_3$): 1.26 (3H, t, $J = 7.5$ Hz, CH_3), 2.66 (1H, d, $J = 5.5$ Hz, H_2), 2.75 (1H, d, $J = 15.5$ Hz, H_{6exo}), 2.90 (1H, dd, $J = 5.5$ and 2.5 Hz, H_5), 3.09 (5H, m, CH_2 and H_{6endo}), 3.60 (3H, s, OMe), 5.22 (1H, dd, $J = 5.5$ and 2.5 Hz, H_3). ^{13}C NMR ($CDCl_3$): 12.4 (CH_3), 30.45 (C_6), 35.4 (C_5), 44.5 (CH_2), 51.7 (C_1), 54.0 (OMe), 58.5 (C_3), 92.5 (C_2), 143.4 (C_4), 224.4 (CO(Mn)). Anal. Calcd: C, 52.67; H, 5.68; N, 4.17. Found: C, 52.45; H, 5.52; N, 4.39.

29 (42%). IR ($CHCl_3$): 1912, 1996 (CO(Mn)). ^1H NMR ($CDCl_3$): 1.89 (3H, s, Me), 2.85 (1H, d, $J = 13$ Hz, H_{6exo}), 2.91 (2H, m, H_{6endo}, H_5), 3.27 (1H, d, $J = 5.5$ Hz, H_2), 3.78 (3H, s, OMe), 4.73 (1H, s, NH), 5.34 (1H, d, $J = 5.5$ Hz, H_3), 6.86 (2H, d, $J = 8$ Hz, Ar H), 7.04 (2H, d, $J = 8$ Hz, Ar H). ^{13}C NMR ($CDCl_3$): 22.4 (Me), 29.8 (C_6), 32.9 (C_5), 55.5 (OMe), 64.0 (C_1), 74.0 (C_3), 105.4 (C_2), 114.7 (Ar CH), 116.6 (Ar CH), 120.7 (C_4), 131.0 (Ar C), 154.3 (Ar CH), 225.6 (CO(Mn)). Anal. Calcd: C, 55.30; H, 4.37; N, 3.79. Found: C, 54.95; H, 4.46; N, 3.48.

Substituting the amine by an alcohol and using NaH as a base instead of cesium carbonate gave access to complexes **30** and **31**. **30** (31%). IR ($CHCl_3$): 1958, 2028 (CO(Mn)). ^1H NMR ($CDCl_3$): 2.16 (1H, d, $J = 12$ Hz, H_{6exo}), 3.25 (2H, m, H_{6endo}, H_5), 3.47 (3H, s, OMe), 3.85 (1H, m, H_2), 6.62 (1H, d, $J = 6$ Hz, H_3), 7.00 (2H, t, $J = 7.5$ Hz, Ar H), 7.20 (2H, d, $J = 7.5$ Hz, Ar H), 7.36 (1H, t, $J = 7.5$ Hz, Ar H). ^{13}C NMR ($CDCl_3$): 25.7 (C_6), 38.8 (C_5), 54.8 (OMe), 65.9 (C_1), 73.0 (C_3), 99.0 (C_2), 116.0 (Ar CH), 125.7 (Ar CH), 129.4 (Ar CH), 144.4 (C_4), 150.9 (Ar C), 222.0 (CO(Mn)). Anal. Calcd: C, 56.50; H, 3.83. Found: C, 56.18; H, 4.14.

31 (38%). IR ($CHCl_3$): 1958, 202 (CO(Mn)). ^1H NMR ($CDCl_3$): 0.80−1.20 (7H, m, CH and CH_3), 1.75 (1H, d, $J = 13$ Hz, H_{6exo}), 2.02 (1H, dd, $J = 13$ and 5.5 Hz, H_{6endo}), 3.17 (1H, dd, $J = 5.5$ and 2 Hz, H_5), 3.31 (2H, m, CH_2), 3.44 (3H, s, OMe), 3.86 (1H, d, $J = 6.5$ Hz, H_2), 5.90 (1H, dd, $J = 6.5$ and 2 Hz, H_3). ^{13}C NMR ($CDCl_3$): 19.6 (CH_3), 25.8 (CH), 27.9 (C_6), 38.7 (C_5), 54.7 (OMe), 71.0 (CH_2), 72.0 and 72.1 (C_1 and C_3), 98.5 (C_2), 143.4 (C_4), 226.8 (CO(Mn)). Anal. Calcd: C, 52.51; H, 5.35. Found: C, 52.23; H, 5.11.

The same procedure conducted with a thiol instead of an alcohol allowed the isolation of complexes **32** and **33a**,**c**,**f**. **32** (73%). IR ($CHCl_3$): 1937, 2021 (CO(Mn)). ^1H NMR ($CDCl_3$): 1.23−1.41 (7H, m, CH_3, CH_2), 2.41 (1H, d, $J = 12$ Hz, H_{6exo}), 2.56 (4H, m, CH_2), 2.86 (1H, dd, $J = 12$ and 6 Hz, H_{6endo}), 3.02 (1H, dd, $J = 6$ and 2.5 Hz, H_5), 3.46 (3H, s, OMe), 4.87 (1H, d, $J = 6$ Hz, H_2), 5.63 (1H, dd, $J = 6$ and 2.5 Hz, H_3). ^{13}C NMR ($CDCl_3$): 17.6 (CH_3), 22.2 (CH_2), 28.5 (C_6), 29.7 (CH_2), 30.8 (CH_2), 32.3 (CH_2), 35.7 (C_5), 54.3 (OMe), 65.8 (C_3), 68.7 (C_1), 94.2 (C_2), 142.6 (C_4), 223.0 (CO(Mn)). Anal. Calcd: C, 51.42; H, 5.47. Found: C, 51.58; H, 5.72.

33a (86%). IR ($CHCl_3$): 1937, 2020 (CO(Mn)). ^1H NMR ($CDCl_3$): 2.33 (3H, s, CH_3), 2.39 (1H, d, $J = 13.5$ Hz, H_{6exo}), 2.73 (1H, dd, $J = 13.5$ and 6.5 Hz, H_{6endo}), 3.13 (1H, d, $J = 6.5$ Hz, H_5), 4.83 (1H, dd, $J = 6.5$ and 5.5 Hz, H_4), 4.93 (1H, d, $J = 5.5$ Hz, H_2), 5.70 (1H, t, $J = 5.5$ Hz, H_3), 7.12 (2H, d, $J = 8$ Hz, Ar H), 7.21 (2H, d, $J = 8$ Hz, Ar H). ^{13}C NMR ($CDCl_3$): 21.2 (CH_3), 30.8 (C_6), 50.7 (C_5), 65.3 (C_1), 96.0 (C_3), 99.0 (C_2), 123.5 (C_4), 128.8 (Ar CH), 130.0 (Ar CH), 132.0 (Ar CH), 132.9 (Ar C), 226.4 (CO(Mn)). Anal. Calcd: C, 56.48; H, 3.85. Found: C, 56.38; H, 4.28.

33c (93%). IR ($CHCl_3$): 1937, 2021 (CO(Mn)). ^1H NMR ($CDCl_3$): 2.31 (3H, s, CH_3), 2.47 (1H, d, $J = 13$ Hz, H_{6exo}), 2.77 (1H, dd, $J = 6$ and 13 Hz, H_{6endo}), 3.02 (1H, d, $J = 6$ Hz, H_5), 3.45 (3H, s, OMe), 4.96 (1H, d, $J = 5.5$ Hz, H_2), 5.64 (1H, d, $J = 5.5$ Hz, H_3), 7.01 (2H, d, $J = 8$ Hz, Ar H), 7.21 (2H, d, $J = 8$ Hz, Ar H). ^{13}C NMR ($CDCl_3$): 21.2 (CH_3), 33.0 (C_6), 36.3 (C_5), 54.5 (OMe), 65.0 (C_1), 66.9 (C_3), 96.2 (C_2), 128.8 (Ar CH), 130.0 (Ar CH), 131.7 (Ar CH), 133.8 (Ar CH), 137.8 (Ar C), 139.7 (Ar C), 142.7 (C_4), 221.3 (CO(Mn)). Anal. Calcd: C, 55.14; H, 4.08. Found: C, 55.12; H, 4.12.

33f (88%). IR ($CHCl_3$): 1937, 2022 (CO(Mn)). ^1H NMR ($CDCl_3$): 2.31 (3H, s, CH_3), 3.44 (3H, s, OMe), 3.48 (1H, dd, $J = 6$ and 3 Hz, H_5), 4.18 (1H, d, $J = 6$ Hz, H_{6endo}), 4.78 (1H, d, $J = 6$ Hz, H_2), 5.55 (1H, dd, $J = 6$ and 3 Hz, H_3), 6.97 (2H, d, $J = 7.5$ Hz, Ar H), 7.06 (2H, d, $J = 7.5$ Hz, Ar H), 7.22 (5H, m, Ar H). ^{13}C NMR ($CDCl_3$): 21.3 (CH_3), 43.8 (C_5), 49.7 (C_6), 54.6 (OMe), 65.0 (C_1), 81.6 (C_3), 91.1 (C_2), 126.4 (Ar CH), 127.2 (Ar CH), 128.4 (Ar CH), 130.0 (Ar CH), 132.5 (Ar C), 135.0 (Ar CH), 139.3 (Ar C), 141.5 (Ar C), 145.2 (C_4), 222.0 (CO(Mn)). Anal. Calcd: C, 61.88; H, 4.29. Found: C, 61.87; H, 4.19.

Using the same procedure with Et_3N as base and P-based nucleophile gave access to complexes **34**, **35**, and **36**. **34** (77%). IR ($CHCl_3$): 1957, 2027 (CO(Mn)). ^1H NMR ($CDCl_3$): 1.28 (6H, t, $J = 9$ Hz, Me), 2.05 (1H, d, $J = 12$ Hz, H_{6exo}), 3.04 (2H, m, H_{6endo}, H_5), 3.42 (3H, s, OMe), 4.12 (5H, m, CH_2. H_2), 5.95 (1H, m, H_3). ^{13}C NMR ($CDCl_3$): 16.7 (CH_3), 27.4 (C_6), 28.8 (CH_2), 37.6 (C_5), 54.6 (OMe), 62.7 (C_1), 71.9 (C_3), 100.4 (C_2), 144.1 (C_4), 217.7 (CO(Mn)). ^{31}P NMR ($CDCl_3$): 28.2. Anal. Calcd: C, 43.7; H, 4.73. Found: C, 43.94; H, 4.92.

For the preparation of **35** (43%) DMF was used instead of THF. IR ($CHCl_3$): 1956, 2021 (CO(Mn)). ^1H NMR ($CDCl_3$): 2.06 (1H, d, $J = 11.5$ Hz, H_{6exo}), 2.91 (2H, m, H_{6endo}, H_5), 3.42 (3H, s, OMe), 5.42 (1H, dd, $J = 5.5$ and 10 Hz, H_2), 5.95 (1H, d, $J = 5.5$ Hz, H_3), 7.40 (4H, d, $J = 8$ Hz, Ar H), 7.56 (4H, t, $J = 8$ Hz, Ar H), 7.72 (2H, t, $J = 8$ Hz, Ar H). ^{13}C NMR ($CDCl_3$): 29.8 (C_6), 36.3 (C_5), 54.6 (OMe), 65.6 (C_1), 71.1 (C_3), 99.7 (C_2), 128.7 (Ar CH), 130.8 (Ar C), 132.0 (Ar CH), 132.1 (Ar CH), 144.3 (C_4), 217.1 (CO(Mn)). ^{31}P NMR ($CDCl_3$): 32.7. Anal. Calcd: C, 59.50; H, 4.05. Found: C, 59.6; H, 4.46.

36 (64%). IR ($CHCl_3$): 1942, 2018 (CO(Mn)). ^1H NMR ($CDCl_3$): 2.26 (1H, d, $J = 13$ Hz, H_{6exo}), 2.77 (1H, dd, $J = 13$ and 6 Hz, H_{6endo}), 2.85 (1H, br d, $J = 6.0$ Hz, H_5), 3.44 (3H, s, OMe), 4.81 (1H, d, $J = 6$ Hz, H_2), 5.80 (1H, dd, $J = 6$ and 2.5 Hz, H_3), 7.19 (6H, m, Ar H), 7.43 (4H, d, $J = 7.5$ Hz, Ar H). ^{13}C NMR ($CDCl_3$): 29.7 (C_6), 35.2 (C_5), 54.4 (OMe), 59.0 (C_1), 68.9 (C_3), 99.1(C_2), 128.5 (Ar CH), 129.5 (Ar CH), 133.4 (Ar

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CH), 134.5 (Ar C), 143.7 (C_4), 219.3 (CO(Mn)). ^{31}P NMR ($CDCl_3$): 59.6. Anal. Calcd: C, 61.12; H, 4.20. Found: C, 61.28; H, 4.20.

Rearomatization. Typical Rearomatization Procedure: Preparation of Complex 37. A solution of triphenyl carbenium tetrafluoroborate (0.173 g, 0.65 mmol) in CH_2Cl_2 (3 mL) was added to a solution of complex **5c** (0.086 g, 0.26 mmol) in CH_2Cl_2 (3 mL). After stirring at room temperature for 1.5 h, the solution was concentrated under N_2 flush. Addition of freshly distilled diethyl ether induced precipitation of ether complex **37**. The yellow solid was obtained by filtration. **37** (93%). IR (CH_3CN): 2025, 2080 (CO(Mn)). ^{1}H NMR (acetone-d_6): 4.23 (3H, s, OCH_3), 6.63 (2H, d, J = 8 Hz, H_3 and H_5), 7.30 (1H, t, J = 4.5 Hz, Ar H), 7.58 (2H, d, J = 8 Hz, H_2 and H_6), 7.86 (1H, d, J = 4.5 Hz, Ar H), 7.97 (1H, d, J = 4.5 Hz, Ar H). ^{13}C NMR (acetone d_6): 59.4 (OMe), 84.2 (C_3 and C_5), 100.7 (C_2 and C_6), 103.2 (C_1), 128.7, 130.3, 131.8 (Ar CH), 135.8 (Ar C), 149.1 (C_4), 216.8 (CO(Mn)). Anal. Calcd: C, 40.42; H, 2.42. Found: C, 40.52; H, 2.59.

The same procedure was applied to the synthesis of complexes **38**, **39*E***, **40b**, **40c**, **41**, **42**, **43**, and **44**.

38 (96%). IR (CH_3CN): 2024, 2079 (CO(Mn)), 2208 (C≡C). ^{1}H NMR (acetone-d_6): 3.84 (3H, s, OMe), 7.00 (2H, d, J = 7.5 Hz, H_3 and H_5), 7.40 (5H, m, Ar H), 7.64 (2H, d, J = 7.5 Hz, H_2 and H_6). ^{13}C NMR (acetone-d_6): 60.0 (OMe), 85.0 (C_3 and C_5), 101.6 (C_2 and C_6), 106.4 (C(C≡C)), 121.0 (C_1), 128.6 (Ar CH), 131.5 (Ar CH), 132.9 (Ar C), 133.5 (Ar CH), 138.6 (C(C≡C)), 148.9 (C_4), 216.8 (CO(Mn)). Anal. (+1 CH_2Cl_2) Calcd: C, 47.15; H, 2.89. Found: C, 46.93; H, 2.76.

39*E* (94%). IR (CH_3CN): 1639 (C═C), 2017 (CO(Mn)). ^{1}H NMR (acetone-d_6) 4.18 (3H, s, OMe), 6.92 (2H, d, J = 7.5 Hz, H_3 and H_5), 7.12−7.64 (9H, m, H_2, H_6, Ar H and H(C═C)). ^{13}C NMR (acetone-d_6): 60.1 (OMe), 85.0 (C_3 and C_5), 101.6 (C_2 and C_6), 106.4 (CH(C═C)), 121.1 (C_1), 128.8 and 129.8 (Ar CH), 130.6 (Ar CH), 135.6 (Ar C), 138.4 (CH(C═C)), 148.9 (C_4), 216.8 (CO(Mn)). Anal. (+1 CH_2Cl_2) Calcd: C, 44.90; H, 3.36. Found: C, 44.98; H, 3.37.

40b (95%). IR (CH_3CN): 2021, 2082 (CO(Mn)), 1720 (CO). ^{1}H NMR (acetone-d_6): 2.73 (3H, s, Me), 6.83 (1H, d, J = 7 Hz, H_3 and H_5), 7.38 (1H, dd, J = 4 and 5 Hz, Ar H), 7.52 (2H, d, J = 7 Hz, H_2 and H_6), 8.07 (1H, d, J = 4 Hz, Ar H), 8.25 (1H, d, J = 5 Hz, Ar H). ^{13}C NMR (acetone-d_6): 20.4 (Me), 98.5 (C_3 and C_5), 103.9 (C_2 and C_6), 110.7 (C_1), 124.2 (Ar C), 130.3 (Ar CH), 138.9 (Ar CH), 139.4 (Ar CH), 141.8 (C_4), 181.9 (CO), 215.4 (CO(Mn)). Anal. Calcd: C, 42.06; H, 2.33. Found: C, 42.06; H, 2.35.

40c (95%). IR (CH_3CN): 2023. 2081 (CO(Mn)), 1720 (CO). ^{1}H NMR (acetone-d_6): 4.27 (3H, s, OMe), 6.58 (1H, d, J = 7.5 Hz, H_3 and H_5), 7.36 (1H, d, J = 4.5 Hz, Ar H), 7.66 (1H, d, J = 7.5 Hz, H_2 and H_6), 8.03 (1H, t, J = 4.5 Hz, Ar H), 8.24 (1H, d, J = 4.5 Hz, Ar H). ^{13}C NMR (acetone-d_6): 58.6 (OMe), 81.3 (C_3 and C_5), 105.3 (C_2 and C_6), 111.2 (C_1), 129.5 (Ar C), 138.0 (Ar CH), 138.5 (Ar CH), 141.1 (Ar CH), 151.7 (C_4), 181.0 (CO), 214.7 (CO(Mn)). Anal. Calcd: C, 40.42; H, 2.42. Found: C, 40.52; H, 2.59.

41 (70%). IR (CH_3CN): 2021, 2080 (CO(Mn)), 1725 (CO). ^{1}H NMR (acetone-d_6): 4.18 (3H, s, OMe), 6.49 (2H, d, J = 2.5 Hz, H_3 and H_5), 7.15 (1H, m, Ar H), 7.33 (2H, d, J = 5.5 Hz, Ar H), 7.37 (2H, d, J = 5.5 Hz, Ar H), 7.69 (2H, d, J = 2.5 Hz, H_2 and H_6). ^{13}C NMR (acetone-d_6): 57.7 (OMe), 81.4 (C_3 and C_5), 104.5 (C_2 and C_6), 111.9 (C_1), 120.7 (Ar CH), 125.7 (Ar CH), 128.6 (Ar CH), 150.2 (Ar C), 159.8 (C_4), 163.0 (CO), 213.0 (CO(Mn)). Anal. Calcd: C, 44.87; H, 2.42. Found: C, 40.52; H, 2.59.

42 (77% two steps). IR (CH_3CN): 2018, 2082 (CO(Mn)), 1718 (CO). ^{1}H NMR (acetone-d_6): 4.08 (3H, s, CO_2Me), 4.28 (3H, s, OMe), 6.56 (2H, d, J = 7 Hz, H_3 and H_5), 7.68 (2H, d, J = 7 Hz, H_2 and H_6). ^{13}C NMR (acetone-d_6): 57.7 (OMe), 62.4 (CO_2-Me), 81.9 (C_1), 86.2 (C_3 and C_5), 109.3 (C_2 and C_6), 154.2 (C_4), 166.3 (CO), 214.6 (CO(Mn)). Anal. Calcd: C, 36.77; H, 2.57. Found: C, 36.34; H, 2.42.

43 (85%). IR (CH_3CN): 2023, 2079 (CO(Mn)), 1705 (CO). ^{1}H NMR (acetone-d_6): 3.67 (8H, m, NCH_2 and OCH_2), 4.18 (3H, s, OMe), 6.40 (1H, d, J = 7.5 Hz, H_3 and H_5), 7.45 (1H, d, J = 7.5 Hz, H_2 and H_6). ^{13}C NMR (acetone-d_6): 51.6 (NCH_2), 61.9 (OMe), 69.8 (OCH_2), 83.8 (C_3 and C_5), 108.6 (C_2 and C_6), 110.2 (C_1), 154.2 (C_4), 164.8 (CO), 218.7 (CO(Mn)). Anal. (+ 1 CH_2Cl_2): Calcd: C, 36.12; H, 3.22; N, 2.63. Found: C, 35.89; H, 3.63; N, 2.88.

44 (65%). IR (CH_3CN): 2030, 2084 (CO(Mn)), 2157 (C≡C), 1667 (CO). ^{1}H NMR (acetone-d_6): 0.35 (9H, s, Me), 4.33 (3H, s, OMe), 6.59 (1H, d, J = 8 Hz, H_3 and H_5), 7.78 (1H, d, J = 8 Hz, H_2 and H_6). ^{13}C NMR (acetone-d_6): −2.0 (Me), 59.0 (OMe), 82.3 (C_3 and C_5), 93.6 and 97.5 (C(C≡C)), 105.2 (C_2 and C_6), 114.2 (C_1), 153.4 (C_4), 171.6 (CO), 215.0 (CO(Mn)). Anal. Calcd: C, 41.95; H, 3.49. Found: C, 42.16; H, 3.61.

45 (35%, two steps). IR (CH_3CN): 2011, 2046 (CO(Mn)), 2233 (CN). ^{1}H NMR (acetone-d_6): 3.72 (3H, s, OMe), 7.76 (2H, d, J = 7 Hz, H_3 and H_5), 7.89 (2H, d, J = 7 Hz, H_2 and H_6). ^{13}C NMR (acetone-d_6): 54.2 (OMe), 77.1 (C_3 and C_5), 121.1 (CN), 131.0 (C_1), 144.0 (C_4), 147.8 (C_2 and C_6), 216.9 (CO(Mn)).

X-ray Crystal Structure Determination for 23, 33f, 40c, and 44. The selected crystals were mounted onto the top of a glass rod. Accurate cell dimensions, orientation matrixes, and data collections were performed at −7 °C for **40c** and at room temperature for the three other compounds, on a Enraf-Nonius MACH-3 diffractometer equipped with graphite-monochromated Mo Kα radiation. No significant variations were observed in the intensities of two checked reflections during data collection for **23**, **33f**, and **44**; however, strong decay was observed for **40c** (44%). This decay was corrected according to standards. More complete crystallographic data, collection parameters, and other significant details are listed in Table 12. Computations were performed by using the PC version of Crystals.[45] The usual corrections for Lorentz and polarization effects were applied. Scattering factors and corrections for anomalous dispersion were taken from International Tables for X-ray Crystallography.[46] The structures were solved by direct methods (SHELXS[47]) and refined by full-matrix least-squares. Non-hydrogen atoms were refined anisotropically excluding the agitated BF_4^- anion and the solvent molecule (acetone) located on the 2-fold axis in **40c**. For these two molecules it was necessary to apply restraints on the bond lengths and angles. In all cases hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter.

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Supporting Information Available: Text giving tables of crystal data, atomic coordinates, and bond distances and angles for complexes **23**, **33f**, **40c**, and **44**. This material is available free of charge via the Internet at http://pubs.acs.org.

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