Selective Access to Electron Donating Group Substituted (η^5-cyclohexadienyl)Mn(CO)$_3$ Complexes by Bimetallic Manganese−Palladium Activation

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Summary: Unprecedented (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes bearing an electron-donating group at the end of the π system have been selectively prepared using Pd catalysis and primary, secondary cyclic, and acyclic amines. This catalytic methodology has been extended to O-, S-, and P-based derivatives. The X-ray structure of one coupling product exhibits an unusual conformation in its η^5 system.

In the course of reactions involving electrophilic η^6-arene metal complexes and nucleophiles,[1] η^5-cyclohexadienyl transition-metal complexes can be isolated or transformed in situ into highly fuctionalized arenes or cyclohexadienes. Those entities coordinated to chromium have been intensively studied, demonstrating their use in organic synthesis.[2]

In contrast, relatively few investigations have been undertaken to exploit the potential of (η^5-cyclohexadienyl)manganese complexes as valuable tools for organic synthesis.[3] This is probably due to the fact that, until recently, the only way to obtain the required (η^5-cyclohexadienyl)manganese complexes consisted of a nucleophilic addition to the parent η^6 complex. Such reactions are known to be efficient with carbon nucleophiles and hydrides.[4,5] Nucleophilic attack on the substituted arene takes place at the 6- or 5-position of the aromatic ring, depending on the electronic effect of a substituent.[6] Electron-withdrawing substituents such as chloride in complex **1** are known to induce mainly an ortho addition, giving complex **2** (Scheme 1, path a).[6b,7] In contrast, electron-donating groups (**4**; Y = OMe, NR$_2$) exclusively direct meta addition, yielding complex **5** (Scheme 1, path b).[3d] Indeed, electronic effects preclude ortho nucleophilic addition and thereby avoid the formation of the 1-substituted η^5-complex **6** (Scheme 1, path c). In other words, no synthesis of (η^5-cyclohexadienyl)manganese complexes substituted with an electron-donating group at the end of the π-system, **6**, had been previously reported. We thought that a possible strategy to prepare these complexes might be found in the reaction of the palladium intermediate **3**, arising from the insertion of Pd(0) into the carbon−chloride bond of (η^5-chlorocyclohexadienyl)manganese complexes **2**,[8] with nucleophiles such as amine, alcoholate, and thiolate in a Buchwald−Hartwig type methodology to afford complex **6** (Scheme 1, path a).[9] Therefore, in this communication we describe an efficient synthesis of previously unknown complexes using a palladium-catalyzed coupling reaction. While elaborate catalytic systems seem to be required and beneficial in Buchwald−Hartwig reactions, the present strategy takes

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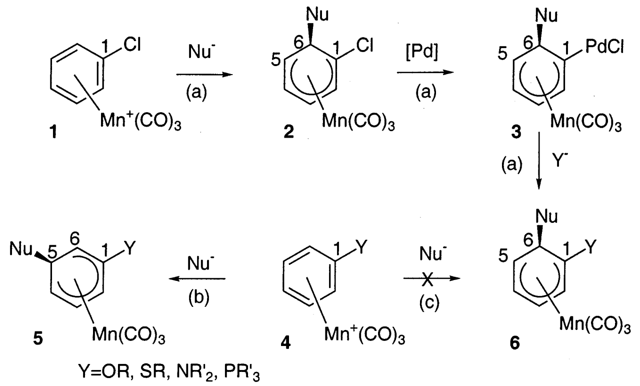
Scheme 1



Scheme 2

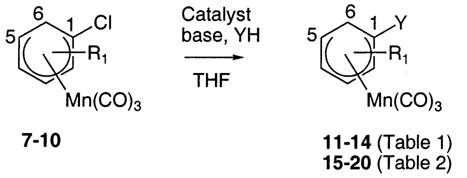


Table 1. Pd-Catalyzed Amination of (η^5-1-chlorocyclohexadienyl)Mn(CO)$_3$ Complexes

entry	complex	YH	complex	yield (%)
1^{a,c}	**7**, R$_1$ = H	HN(CH$_2$CH$_2$)$_2$O	**11**	84
2^{b,c}	**7**, R$_1$ = H	HN(CH$_2$CH$_2$)$_2$O		0
3^{a,c}	**8**, R$_1$ = 4-OMe	HNEt$_2$	**12**	84
4^{a,c}	**9**, R$_1$ = 4-Me	H$_2$NPh-4-OMe	**13**	42
5^{a,c}	**10**, R$_1$ = 2-OMe	HN(CH$_2$CH$_2$)$_2$O	**14**	0

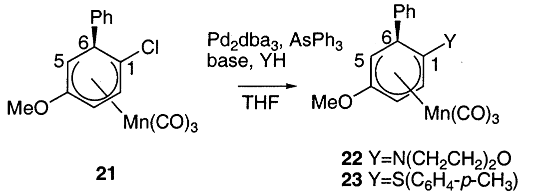
^{a} Catalyst: Pd$_2$dba$_3$, AsPh$_3$. ^{b} Without catalyst. ^{c} Base: Cs$_2$CO$_3$.

Table 2. Pd-Catalyzed Reaction of (η^5-1-chlorocyclohexadienyl)Mn(CO)$_3$ Complexes with Alcohol, Thiols, Phosphine, and Phosphite Oxide

entry	complex	YH	complex	yield (%)
1^{a,b}	**8**	isoamyl-OH	**15**	37
2^{a,b}	**8**	*p*-tolyl-SH	**16**	93
3^{a,b}	**8**	C$_5$H$_{11}$SH	**17**	73
4^{a,b}	**7**	*p*-tolyl-SH	**18**	81
5^{a,c}	**9**	(EtO)$_2$P(O)H	**19**	77
6^{a,c}	**10**	PPh$_2$H	**20**	65

^{a} Catalyst: Pd$_2$dba$_3$,AsPh$_3$. ^{b} Base: NaH. ^{c} Base: Et$_3$N.

Scheme 3



advantage of the use of a simple Pd/AsPh$_3$ [10] catalytic combination.

The requisite (η^5-1-chlorocyclohexadienyl)Mn(CO)$_3$ complexes **7**−**10** were readily prepared by hydride addition to the parent (η^6-chloroarene)Mn(CO)$_3^+$ complexes, as already described.[11] In a preliminary experiment, morpholine and Cs$_2$CO$_3$ were added to premixed complex **7**, Pd$_2$(dba)$_3$, and AsPh$_3$ in freshly distilled and degassed THF under a nitrogen atmosphere (Scheme 2). Complete disappearance of the starting material was observed over 6 h at 60 °C, giving rise to the formation of **11** in 84% yield (Table 1, entry 1). A control experiment conducted under the same reaction conditions but without using a catalyst gave no reaction (entry 2). These initial results prompted us to extend this strategy to different substituted starting materials and a variety of amines. Indeed, the (η^5-1-chloro-4-substituted cyclohexadienyl)Mn(CO)$_3$ complexes **8** and **9** underwent amination using secondary and primary amines, respectively (entries 3 and 4). Only complex **10** did not display the expected amination product, probably due to steric hindrance (entry 5).

Next we examined the palladium-catalyzed reactions of various heteronucleophiles such as O-, S-, and P-based derivatives (Table 2). Preformed sodium isoamylate reacted with complex **8** under the aforementioned conditions to afford the corresponding ether, **15**, in 37% yield (entry 1). Alkyl and aryl thioethers **16**−**18** were isolated in better yields (73−93%) using the same methodology (entries 2−4). Extension of this methodology to P-based nucleophiles was also successful. Indeed, diethyl phosphite oxide and diphenylphosphine gave the corresponding complexes **19** and **20** in 77 and 65% yields, respectively (entries 5 and 6). Reactions involving P-based nucleophiles require the use of triethylamine instead of NaH as a base.

Taking advantage of these observations, we have carried out further investigations using complex **21**, in which the sp^3 carbon is substituted by a phenyl group.[12] Combinations of morpholine/Cs$_2$CO$_3$ and *p*-tolylSH/NaH under palladium catalysis were effective for the introduction of a nucleophile at position 1 (Scheme 3). No problem with steric hindrance was detected. Complexes

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(12) Complex **21** was prepared according to the procedure described in ref 7.

(13) A typical procedure for the Pd-catalyzed reaction is given by the preparation of complex **16**: Pd$_2$(dba)$_3$ (0.029 g, 0.03 mmol) and AsPh$_3$ (0.34 g, 0, 11 mmol) were added to a solution of complex **2** (0.089 g. 0.32 mmol) in anhydrous degassed THF (10 mL). After 15 min at room temperature, a THF solution of *p*-methylthiophenol (0.040 g, 0.32 mmol) and NaH (0.005 g, 0.38 mmol) was introduced. The reaction mixture was refluxed overnight, poured into cold water (100 mL), and extracted with 50 mL of pentane; the organic phase was washed with water (2 × 20 mL), dried over magnesium sulfate, and filtered. Solvents were evaporated under a nitrogen flush. The residue obtained was purified by silica gel chromatography (pentane) to deliver complex **16** as a yellow solid in 93% yield. IR (CH$_2$Cl$_2$): ν(CO) 1917, 1998 cm^{-1}. ^{1}H NMR (CDCl$_3$; 200 MHz): δ 2.91 (dd, J = 13 and 6.5 Hz, 1H, H-6 endo), 2.48 (d, J = 13 Hz, 1H, H-6 exo), 2.32 (s, 3H), 3.01 (d, J = 6.5 Hz, 1H, H-5), 3.45 (s, 3H), 4.96 (d, J = 5.5 Hz, 1H, H-2), 5.65 (d, J = 5.5 Hz, 1H, H-3), 7.10 (d, J = 8 Hz), 7.21 (d, J = 8 Hz). ^{13}C NMR (CDCl$_3$; 100 MHz): δ 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, 130.0, 131.7, 133.8, (C_6H$_4$), 142.7 (C-4), 221.3 (CO). Anal. Calcd: C, 55.14; H, 4.08. Found: C, 55.12; H, 4.10. Crystal data for **16**: C$_{17}$H$_{15}$MnO$_4$S, M_r = 370.3, orthorhombic, space group $P2_12_12_1$, a = 8.463(2) Å, b = 13.716(6) Å, c = 14.385(3) Å, D_c = 1.47 g cm^{-3}, Z = 4, crystal size 0.10 × 0.40 × 0.40 mm, μ = 8.94 cm^{-1}, 2325 data collected at 295 K (θ range 1−28°) on an Enraf-Nonius CAD-4 diffractometer. An absorption correction using DIFABS ($T_{\min}$ = 0.65, $T_{\max}$ = 1) was applied. Anomalous dispersion terms and correction of secondary extinction were applied. The structure was solved by direct methods (SHELXS) and refined on F (CRYSTALS) by least-squares analysis using anisotropic thermal parameters for all non-hydrogen atoms. H atoms were introduced in calculated positions and were allocated an overall isotropic thermal parameter. A total of 1356 reflections with $I > 3\sigma(I)$ were used to solve and refine the structure to R = 0.0445 and R_w = 0.0516, 210 least-squares parameters, GOF = 1.02.

22 and **23** were isolated in 55 and 91% yields, respectively.

Well-formed crystals suitable for X-ray analysis were obtained after crystallization of complex **16** from a hexane/diethyl ether mixture.[13] The structure undoubtedly confirmed the regioselectivity of the reaction. Interestingly, the η^5-cyclohexadienyl moiety did not exhibit the expected classical five-coplanar-carbon geometry (C_1, C_2, C_3, C_4, C_5)[14] with one carbon, C_6, lying out of this plane. Rather, we observed that two carbons, C_6 and C_2, are located out of the plane formed by the other C_1, C_3, C_4, and C_5 sp^2 carbons and away from the metal center. Indeed, the $Mn-C_1/C_3/C_4/C_5$ bond lengths lie between 2.15 and 2.20 Å, whereas $Mn-C_2$ and $Mn-C_6$ bonds manifest lengths of 2.38 and 2.48 Å, respectively. The dihedral angles between the C_1,C_3,C_4,C_5/C_1,C_2,C_3 and C_1,C_3,C_4,C_5/C_1,C_5,C_6 planes reach 19.8 and 25.2°, respectively.

This could be better described as a π-allyl C_3, C_4, C_5 σ-alkyl C_1 derivative[15] which might be represented by a "high-heeled-shoe" conformation, as shown in Figure 1. For the moment it is difficult to explain this unexpected structure, and we can only suggest that the thiophenyl residue might play an important role in forcing the complex to adopt this conformation in the solid state.

In conclusion, we have successfully developed a general palladium-catalyzed approach to new (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes bearing electron-donating groups at the terminus of the π-system. These complexes cannot be synthesized using classical methods. An X-ray structure of one of the C_1-substituted cyclohexadienyl manganese compounds shows an unusual conformation which contravenes the "rule" of planarity among the five sp^2 carbons. Further investigations on the structural and chemical properties of such compounds are currently in progress.

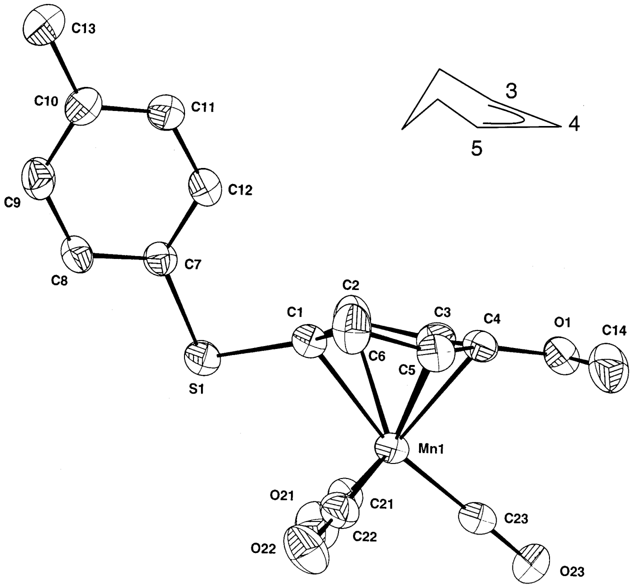

Figure 1. X-ray structure of complex **16** with the numbering scheme and the "high heeled-shoe" analogy. Thermal ellipsoids are presented at the 30% probability level. Selected bond lengths (Å) and angles (deg): $Mn-C_1 = 2.17$, $Mn-C_2 = 2.38$, $Mn-C_3 = 2.15$, $Mn-C_4 = 2.20$, $Mn-C_5 = 2.17$, $Mn-C_6 = 2.46$; $[C_1C_2C_3]/[C_1C_3C_4C_5] = 19.8$, $[C_1C_5C_6]/[C_1C_3C_4C_5] = 25.5$.

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Supporting Information Available: Text giving spectral data for the new compounds and tables of crystal data, atomic coordinates, and bond distances and angles for complex **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] For X-ray studies of (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes, see for example: (a) Lee, T. Y.; Bae, H. K.; Chung, Y. K.; Hallowse, W. A.; Sweigart, D. A. *Inorg. Chim. Acta* **1994**, *224*, 147. (b) Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D. A. *Chem. Eur. J.* **1997**, *3*, 75. (c) Balssa, F.; Gagliardini, V.; Lecorre-Susanne, C.; Rose-Munch, F.; Rose, E.; Vaissermann, J. *Bull. Chem. Soc. Fr.* **1997**, *134*, 537. (d) Renard, C.; Valentic, R.; Rose-Munch, F.; Rose, E. *Organometallics* **1998**, *17*, 1587. (e) Rose, E.; Lecorre-Susanne, C.; Rose-Munch, F.; Renard, C.; Gagliardini, V.; Tedji, F.; Vaissermann, J. *Eur. J. Inorg. Chem.* **1999**, *3*, 421. (f) Son, S. U.; Paik, S. J.; Park, K. H.; Lee, Y. A.; Lee I. S.; Chung, Y. K., Sweigart, D. A. *Organometallics* **2002**, *21*, 239.

[15] One of the reviewers mentioned an interesting example of a σ,π-cyclohexenyl complex of Mn (Pike, R. D.; Ryan, W. J.; Lennhoff, N. S.; Van Epp, J.; Sweigart, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 4798) presenting a striking resemblance to that described here. However, in this structure, C2 atom is an sp^3 carbon not bonded to the Mn atom.