First Synthesis of Cationic [(η^6-arene)Mn(CO)$_3$] Complexes Substituted by Resonance Electron Withdrawing Groups

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Summary: An unprecedented class of cationic [(η^6-RCO-arene)Mn(CO)$_3$] complexes bearing resonance electron withdrawing groups have been synthesized by a high-yield two-step methodology starting from the neutral (η^5-1-chlorocyclohexadienyl)Mn(CO)$_3$ complex, employing a facile and selective transition-metal-catalyzed carbonylation followed by rearomatization. Definitive spectroscopic details of the novel [(η^6-RCO-arene)Mn(CO)$_3$]$^+$ products are discussed, and in one case (R = PhO), the structure has been confirmed by X-ray crystallography.

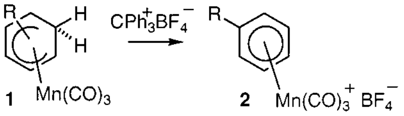
Complexation of arenes alters their chemical reactivity and provides a useful synthetic methodology to prepare functionalized arenes and cyclohexadienes.[1,2] In particular, η^6 coordination of aromatic molecules to the cationic Mn(CO)$_3^+$ moiety activates the arene ring toward nucleophilic addition, affording neutral η^5-cyclohexadienyl complexes which can release the free arenes upon oxidative removal of the metal.[2]

The main synthetic methods reported for the preparation of such cationic complexes involve the direct coordination of arenes to the Mn(CO)$_3$ residue by using Mn(CO)$_5$Br[3a] or Mn$_2$(CO)$_{10}$[3a] or by transferring Mn(CO)$_3^+$ from cationic (polyarene)Mn(CO)$_3^+$ complexes.[3b,c]

Thus, arenes bearing electron donating substituents such as alkyl, alkoxy, and hydroxy may be coordinated in high yield. Even arenes with only moderately accepting groups such as aryl, chloride, or nonconjugated carbonyl groups can be coordinated as well,[3a] but, to the best of our knowledge, there is no report of the preparation of Mn complexes of arenes substituted by strongly electron withdrawing groups that accept electron density through resonance effects.

The failure of the complexation of such arenes has to be attributed to electron deficiency of the ring. Furthermore, unlike the corresponding Cr complexes,[4] even when the resonance electron withdrawal of the keto group is disrupted by the formation of a ketal, for example, no coordination occurred.[3a]

Consequently, we have tried to develop a strategy for the synthesis of such complexes. The approach adopted takes advantage of the particular property of η^5-cyclohexadienyl complexes **1**[5] that easily undergo *exo* hydride abstraction at the sp^3 carbon, thus forming the corresponding cationic η^6 complexes **2** (eq 1).[6]



(1)

Thus, our aim was, first, the preparation of η^5 neutral complexes substituted by electron-withdrawing groups such as a keto, an ester, an amide, or a cyano group and, second, their rearomatization. This communication describes a successful two-step methodology that gives access to unprecedented (η^6-arene)Mn$^+$(CO)$_3$ complexes substituted by resonance electron withdrawing groups and characterization details of the products. Our approach is based on palladium-catalyzed carbonylation reactions at C−Cl positions π-bound to manganese.

Recently the unique behavior of the Pd$_2$(dba)$_3$/AsPh$_3$ catalytic system has been applied successfully in organometallic compounds. Indeed, it allows new synthetic transformations which failed or were much less effective when phosphine-based ligands were used. Examples include the preparation of new (η^6-RCO-arene)Cr(CO)$_3$ complexes under mild conditions[7] and selective substitution of halogens in (η^5-chlorocyclohexadienyl)Mn(CO)$_3$ complexes.[8] Unfortunately, all our attempts to extend

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[1] See for example: (a) Astruc, D. In *Chimie Organométallique*; EDP Sciences: Les Ulis, France, 2000; Chapter 3-6, p 87. (b) Rose-Munch, F.; Rose, E. *Current Org. Chem.* **1999**, *3*, 445 and references therein. (c) Rose-Munch, F.; Gagliardini, V.; Renard, C.; Rose, E. *Coord. Chem. Rev.* **1998**, *178−180*, 249. (d) Semmelhack, M. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, p 979.

[2] McDaniel, K. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 6, p 93.

[3] (a) For the scope of (η^6-arene)Mn(CO)$_3$ synthesis, see for example: Jackson, J. D.; Villa, S. J.; Bacon, D. S.; Pike, R. D.; Carpenter, G. B. *Organometallics* **1994**, *13*, 3972 and references therein. (b) Lee, S. S.; Lee, T. Y.; Lee, I. S.; Chung, Y. K.; Lah, M. Soo. *Organometallics* **1996**, *15*, 3664. (c) Sun, S.; Yeung, L. K.; Sweigart, D. A.; Lee, T. Y.; Lee, S. S.; Chung, Y. K.; Switzer, S. R.; Pike, R. D. *Organometallics* **1995**, *14*, 2613.

[4] (a) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154. (b) Kondo, Y.; Green, J. R.; Ho, J. *J. Organomet. Chem.* **1993**, *58*, 6182.

[5] Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1677.

[6] Woo, K.; Williard, P. G.; Sweigart, D. A.; Duffy, N. W.; Robinson, B. H.; Simpson, J. *J. Organomet. Chem.* **1995**, *487*, 111.

[7] Prim, D.; Tranchier, J. P.; Rose-Munch, F.; Rose, E.; Vaissermann, J. *Eur. J. Inorg. Chem.* **2000**, *5*, 901.

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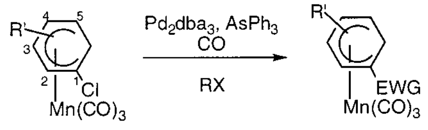
Table 1. Substitution of Chloride Atom by an Electron-Withdrawing Group



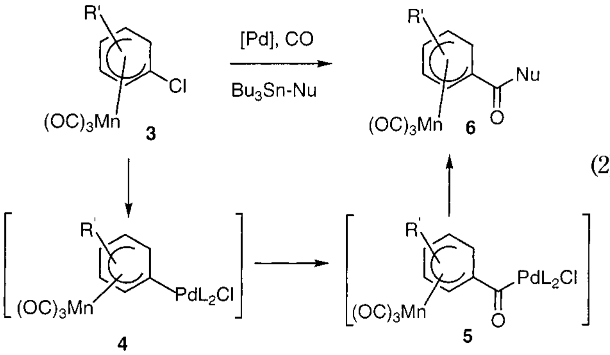
3 **6**

R' = Me, OMe

entry	R′	**3**	RX	yield (%)	**6**	EWG
1	4-Me	**3a**	thienyl-2-$SnBu_3$	90^a	**6a**	COTh
2	4-MeO	**3b**	thienyl-2-$SnBu_3$	90^b	**6b**	COTh
3	4-Me	**3a**	Bu_4Sn	56^a	**6c**	COBu
4	4-MeO	**3b**	Bu_4Sn	45^a	**6d**	COBu
5	4-Me	**3a**	Bu_3SnH		**6e**	CHO
6	4-MeO	**3b**	PhONa	71^a	**6f**	CO_2Ph
7	4-MeO	**3b**	$HN(CH_2CH_2)_2O$	48^a	**6g**	$CON(CH_2CH_2)_2O$

[a] Reaction time 2 h. [b] Reaction time 6 h.

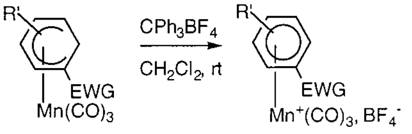
such catalytic transformations to cationic tricarbonyl(η^6-chloroarene)manganese complexes have failed up to now;[9] therefore, we turned instead to investigate first the transition-metal-catalyzed carbonylation of a series of (η^5-chlorocyclohexadienyl)$Mn(CO)_3$ complexes **3** under a CO atmosphere in the presence of $Pd_2(dba)_3$, $AsPh_3$,[10] and stannous derivatives as a source of the second substituent (Nu, eq 2) on the electron withdrawing end group (EWG) of the products.



(2)

In the case of 2-(tributylstannyl)thiophene (RX = $SC_4H_3SnBu_3$), after the reaction mixture was refluxed for 2 h, the thienyl ketone **6a** was obtained in 90% yield (Table 1, entry 1). The reaction has to be undertaken carefully under a CO atmosphere during the entire process. Indeed, if CO is introduced only after the addition of RX, a direct coupling compound may be isolated as a byproduct in yields ranging from 5% to 20%. The same reaction performed with the η^5-1-chloro-4-methoxycyclohexadienyl complex **3b** afforded the thienyl ketones **6b** in 90% yield (Table 1, entry 2).[11] This reaction has been extended to another stannous derivative, $SnBu_4$. Under the same conditions, complexes **3a** and **3b** afforded alkyl ketones **6c** and **6d** in 56 and 45% yields, respectively (Table 1, entries 3 and 4). In the case of **3a** and Bu_3SnH, however, we never observed the expected formation of the aldehyde **6e** (Table 1, entry 5) even by changing the experimental conditions.

Table 2. Aromatization of η^5-Cyclohexadienyl Complexes



6 **7**

entry	R′	**6**	EWG	yield (%)	**7**
1	4-Me	**6a**	COTh	95^a	**7a**
2	4-MeO	**6b**	COTh	85^b	**7b**
3	4-MeO	**6f**	CO_2Ph	70^a	**7f**
4	4-MeO	**6g**	$CON(CH_2CH_2)_2O$	85^a	**7g**

[a] Reaction time 3 h. [b] Reaction time 15 h.

Table 3. Selected ^{1}H NMR^a Data of Complexes 6 and 7

complex	$\delta(H_2)$	$\delta(H_3)$	$\Delta\delta^b$	complex	$\delta(H_2)$	$\delta(H_3)$	$\Delta\delta^b$
6a	6.01^c	6.01^c	0.00	**7a**	7.52	6.83	0.69
6b	6.03	6.14	0.11	**7b**	7.66^d	6.57^e	1.09^f
6f	6.03	6.12	0.08	**7f**	7.69	6.49	1.20
6g	5.43	5.81	0.38	**7g**	7.43	6.40	1.03
6h	5.08	6.07	0.99	**7h**	7.90	7.74	0.14

[a] $CDCl_3$. [b] $\Delta\delta = \delta(H_2) - \delta(H_3)$. [c] Broad. [d] δ 7.89 for the free arene. [e] δ 6.97 for the free arene. [f] In the case of the corresponding chromium complex[7] this difference was found to be 1.13.

We propose that these ketones **6a**–**d** are most probably formed via the postulated intermediate **4**, which can undergo CO insertion to give the acylpalladate complex **5**. This mechanistic postulate provides a possibility to extend the reaction to the preparation of carboxylic acid derivatives. For this purpose, we tried to trap the intermediate **5** with classical nucleophiles[12] in order to have an access to esters and amides. PhONa as well as morpholine reacted with complex **3b**, giving the corresponding ester **6f** and amide **6g** in 71% and 48% yields, respectively (Table 1, entries 6 and 7).

At this point it was crucial to know if it was possible to perform the aromatization of these η^5 derivatives.[13] This was achieved by reaction with CPh_3BF_4 in CH_2Cl_2, and the required cationic complexes **6a,b,f,g** were obtained in 95, 85, 70, and 85% yields, respectively (Table 2).

Selected ^{1}H NMR data of η^5 and η^6 complexes (Table 3) show that the differences of chemical shifts $\Delta\delta = \delta(H_2) - \delta(H_3)$ of these complexes are small in the case of the η^5 derivatives and positive and very large in the case of the η^6 complexes (up to 1.20 ppm; Table 3). This suggests a synergistic effect of the electron withdrawing group favoring an *anti*-eclipsed conformation of the tripod $Mn(CO)_3$, whereas the electron-donating MeO group favors the eclipsed conformation, as is already known for analogous Cr complexes.[1]

Cationic arene–Mn complexes are usually described as amorphous powders[14] which are difficult to crystal-

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[9] Carpentier, J. F.; Castanet, Y.; Brocard, J.; Mortreux, A.; Rose-Munch, F.; Susanne, C.; Rose, E. *J. Organomet. Chem.* **1995**, *493*, C22.

[10] Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434.

[11] In the case of the more crowded (η^5-1-chloro-2-methyl)cyclohexadienyl complex, no coupling reaction occurred.

[12] See for example: (a) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158. (b) Torraca, K. E.; Kuwabe, S.-I.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 12907. (c) Shelby, Q.; Kataoka, N.; Mann, G.; Hartwig, J. *J. Am. Chem. Soc.* **2000**, *122*, 10718.

[13] Reaction of complex **3b** with KCN in DMF at 60 °C for 8 h afforded the corresponding nitrile **6h** (R′ = 4-OMe, EWG = CN), which was very difficult to purify from the crude mixture. However, treating directly the reaction mixture with CPh_3BF_4 in CH_2Cl_2, we succeeded in isolating the pure complex **7h** (R′ = 4-OMe, EWG = CN) in an overall yield of 35% (from **3b**).

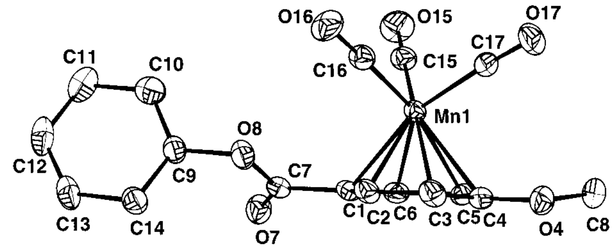

Figure 1. Molecular structure of **7f** (molecule a). Selected bond lengths (Å) and angles (deg): C1−C7 = 1.494(7), Mn1−C1 = 2.154(4), Mn1−C4 2.273(5), C7−O7 = 1.191(6); C1−C7−O7 = 123.7(4), O7−C7−O8 = 125.2(4).

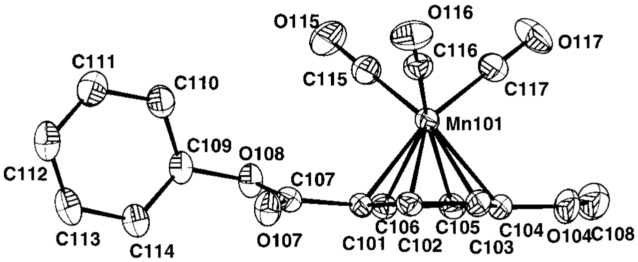

Figure 2. Molecular structure of **7f** (molecule b). Selected bond lengths (Å) and angles (deg): C101−C107 = 1.486(7), C107−O107 = 1.180(6), Mn101−C101 = 2.161(4), Mn101−C104 = 2.266(5); C101−C107−O107 = 111.1(4), O107−C107−O108 = 124.5(5).

lize, but after many attempts, we finally succeeded in obtaining well-formed, very stable yellow crystals of complex **7f** whose structure was determined by an X-ray study.[15]

In this structure, the asymmetric unit consists of two independent molecular cations (labeled a and b) and two independent BF_4 anions (Figures 1 and 2). The conformations of the two $Mn(CO)_3$ tripods are not identical. In molecule a, the structure shows an eclipsed $Mn(CO)_3$ conformation with respect to the methoxy group (Figure 1), whereas a slightly more deviated conformation is observed in molecule b (Figure 2), the Mn−CO bond being rotated by 5 and 17° from carbons C4 and C104, respectively.[16]

It is interesting to note that the C=O double bond is not parallel to the plane of the Mn-bound arene but points out in the direction opposite to the $Mn(CO)_3$ entity with dihedral angles of 28 and 15° in molecules a and b, respectively.

In conclusion, we were able to prepare unprecedented $[(\eta^6\text{-arene})Mn(CO)_3]^+$ complexes substituted by resonance electron withdrawing groups using a two-step methodology to overcome the impossibility of direct complexation. These compounds should have exceptional reactivity, as they possess three highly electrophilic sites: the $Mn(CO)_3$ entity, the complexed arene ring, and, finally, the acyl group. Our results open the way to explore new perspectives in the reactivity of such complexes, and their potential applications in organic synthesis as well as in material science are being actively studied.

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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 compound **7f**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010162J

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(14) Pearson, A. J.; Zhu, P. Y.; Youngs, W. J.; Bradshaw, J. D.; McConville, D. B.; *J. Am. Chem. Soc.* **1993**, 115, 10376.

(15) Crystal data: $C_{17}H_{12}BF_4MnO_6$, $M_r = 454$, triclinic, space group $P\bar{1}$, $a = 10.227(7)$ Å, $b = 10.284(6)$ Å, $c = 18.704(6)$ Å, $\alpha = 77.90(5)°$, $\beta = 78.84(6)°$, $\gamma = 84.49(5)°$, $D_c = 1.60$ g cm^{-3}, $Z = 4$, crystal size 0.06 × 0.40 × 1.00 mm, $\mu = 7.40$ cm^{-1}, 7014 data collected at 266 K on an Enraf-Nonius MACH3 diffractometer. An absorption correction using DIFABS ($T_{min} = 0.72$, $T_{max} = 1$) was applied. Anomalous dispersion terms and no correction of secondary extinction were applied. The structure was solved by direct methods (SHELXS) and refined (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 4329 reflections with $I > 3\sigma(I)$ were used to solve and refine the structure to $R = 0.0556$ and $R_w = 0.0678$: 525 least-squares parameters, GOF = 1.10.

(16) This value is very close to the value of the corresponding angle in the $CH_3CO_2-C_6H_5Cr(CO)_3$ complex: Saillard, J. Y.; Grandjean, D. *Acta Crystallogr.* **1976**, *B32*, 2285.