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Heteropolymetallic Complex Syntheses by Reiterative Nucleophilic Additions of Lithiated (η^6-Arene)tricarbonylchromium Compounds to Cationic (η^6-Benzene)manganese Complexes

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Treatment of lithiated (η^6-X_n-substituted-arene)$Cr(CO)_3$ complexes ($X = OMe$, $n = 2, 3$) with (η^6-benzene)$Mn(CO)_xL_{3-x}$ PF_6 complexes ($L = P(OEt)_3$, $x = 0, 1$) gave rise to the formation of di-, tri-, and tetrapolymetallic complexes depending on the experimental conditions. A “one-pot” procedure was developed to obtain tetranuclear complexes directly from (η^6-arene)-Cr and -Mn mononuclear complexes. The molecular structures of the trinuclear complex **5b** ($(CO)_3Cr[\mu$-η^6-1,3-$(OCH_3)_2$-C_6H_2:$(\eta^5$-$C_6H_6)_2]Mn_2[(CO)_4(P(OEt)_3)_2]$) and of tetranuclear complex **9** ($(CO)_3Cr[\mu$-η^6-1,3,5-$(OCH_3)_3$-C_6:$(\eta^5$-$C_6H_6)_3]Mn_3[(CO)_6(P(OEt)_3)_3]$) have been determined by X-ray crystallography.

Introduction

Arenes can be easily coordinated to neutral tricarbonylchromium or cationic tricarbonylmanganese entities giving neutral (η^6-arene)tricarbonylchromium or more electrophilic cationic (η^6-arene)tricarbonylmanganese complexes.[1] Several studies have focused on the addition of “classical” nucleophiles to the arene ring of these manganese complexes. These nucleophiles include carbanion enolates, Grignard reagents, α-cyano- or α-nitrocarbanions,[2−9] diazo groups,[10] and phosphonates.[11] In contrast, a small number of investigations have used organometallic derivatives as nucleophiles.[12] One of the few areas which have been studied is that of benzylic and homobenzylic anions. Indeed, Beck et al. described the reaction of (η^6-benzene)tricarbonylmanganese with deprotonated diphenyl methane or benzothiophene coordinated to tricarbonylchromium.[13] They also observed the reactions with carbonyl osmate,[14] carbonyl rhenate,[15] and anionic alkynyl complexes.[12e] Our own contributions have been aimed at studying the

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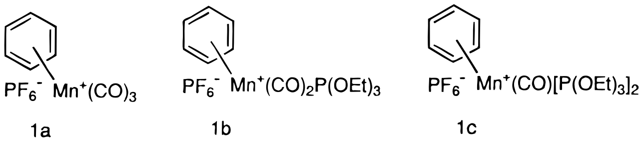
Chart 1



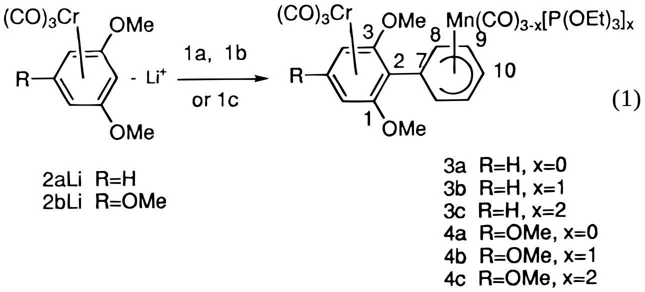
reactivity of cationic (η^6-arene)tricarbonylmanganese toward Fischer-type carbene anions.[16] (Arene)tricarbonylchromium complexes are known to be easily deprotonated,[1d] so we decided to study the reactivity of such organometallic aryllithium derivatives[17] with cationic (η^6-arene)tricarbonylmanganese complexes. We report herein the reaction of lithiated alkoxy-substituted (arene)tricarbonylchromium complexes with cationic (η^6-benzene)tricarbonylmanganese, thus demonstrating the potential of this method in the syntheses of heteropolymetallic compounds, which could hold a pivotal role in the development of polynuclear organometallic chemistry.[18]

Studies and applications of ring deprotonation of (η^6-arene)tricarbonylchromium complexes have mainly employed strong bases such as *n*-BuLi.[1e] Fluoro and alkoxy substituents have been shown to give high to very high ortho selectivity,[19] however, *meta* substitution was observed when the arene ring was substituted by very bulky groups.[20] But fluoroarenetricarbonylchromium derivatives are known to be synthesized with low yield because of their electron-deficient ring. For these reasons, we chose polymethoxy-substituted arene complexes such as 1,3-dimethoxy- and 1,3,5-trimethoxy(η^6-benzene)tricarbonylchromium complexes as the starting material.

Results and Discussion

Dinuclear Complexes. Complex **2a** was obtained by a facile monolithiation at carbon 2 due to the synergistic effects of the two heteroatoms (no formation of disubstitution products[21] was detected).

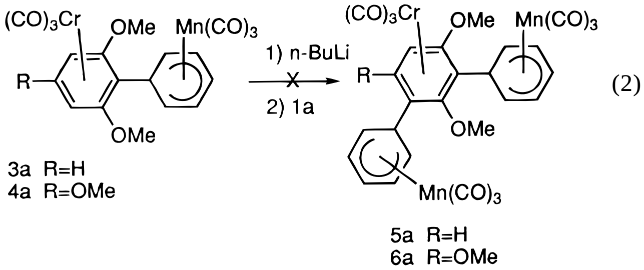
Addition of complex **2a** (obtained by deprotonation of the corresponding neutral complex by 1.1 equiv of *n*-BuLi) to 1.2 equiv of benzenetricarbonylmanganese (**1a**) (Chart 1) gave an 80% isolated yield of the dinuclear complex **3a** (eq 1). The same reaction using 2-lithio-1,3,5-trimethoxy complex **2bLi** as the nucleophile gave rise to the formation of complex **4a** in 72% yield.



(1)

Both the IR spectra (ν(CO) 1875, 1920, 1955, and 2005 cm^{-1} for **3a**; ν(CO) 1865, 1935, 1955, and 2015 cm^{-1} for **4a**) and the NMR spectroscopic data (δ CO), 223.2 (Mn), 233.7 (Cr) ppm for **3a**; 223.4 (Mn), 234.1 (Cr) ppm for **4a**) with nicely distinct signals for the manganese ring protons (the ^{1}H NMR spectrum for **3a**, for example, exhibits a multiplet for H8 and H12 at δ 2.70 ppm, a triplet for H9 and H11 at δ 5.02 ppm, and a triplet of triplets for H10 at δ 5.82 ppm) and chromium ring protons (the ^{1}H NMR spectrum for **3a** exhibits a triplet for H5 at δ 5.57 ppm and a doublet for H4 and H6 at δ 4.62 ppm) agreed with such structures. Furthermore, the multiplicity of the H7 protons (triplet at δ 4.36 ppm for **3a**, triplet at δ 4.24 ppm for **4a**) confirmed the exo addition of the nucleophile (aryllithium−Cr) with respect to the $Mn(CO)_3$ entity.

We attempted to take advantage of the presence of the other acidic protons (ortho to the methoxy groups) in complexes **3a** and **4a** to synthesize, by the same pathway, the tri- and tetrapolymetallic complexes. Complex **3a** (or **4a**) was subsequently converted into the corresponding lithiated arene (eq 2), which gave, after addition to a solution of **1a**, a black mixture which was certainly due to the formation of unstable products. It was impossible to isolate the expected complex **5a** (or **6a**) (eq 2).



(2)

It has been observed that single electron transfer[6e,22] or CO attack[6n] could afford unstable products. If this was the case, we reasoned that the problems could be circumvented by replacing one of the CO ligands in **1a**

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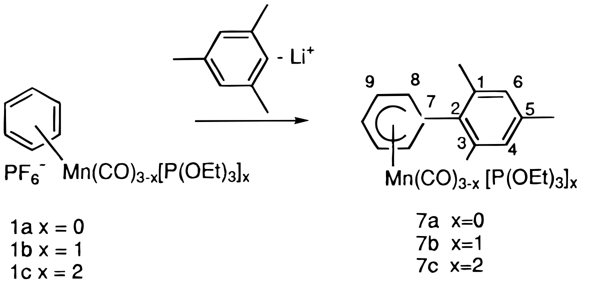
Table 1. Shielding Effect of Phosphito Ligands on the η^5-Cyclohexadienyl Protons of Complexes 3a, 3b, 3c, 4a, 4b, and 4c

	δ (ppm)		
complex	H10	H9, H11	H8, H12
3a	5.82	5.02	3.47
3b	5.49	4.77	3.11
3c	5.15	4.64	2.70
4a	5.76	4.95	3.42
4b	5.49	4.79	3.07
4c	5.16	4.65	2.68

with a phosphito ligand.[23] The resulting complex **1b** (Chart 1) should be more difficult to reduce. Furthermore, the increased steric hindrance at the manganese atom would force the nucleophilic attack to occur on the arene ring, thus inhibiting detrimental side reactions.

This last assessment was provided by the results obtained from studying the reactivity of mesityllithium toward the three cationic benzenemanganese complexes: **1a**, **1b**, and **1c**. The last two were prepared by substitution of one or two of the CO ligands by one or two triethylphosphito ligands, respectively. In the three cases, we observed the formation of η^5-cyclohexadienyl complexes **7** due to the addition of the aryllithium to the manganese ring (eq 3). The yields increased from 38% (for $x = 0$) to 54% ($x = 1$) and finally to 74% ($x = 2$). In other words, the sterically hindered manganese entity favored nucleophilic attack on the arene ring. In light of these results, it was interesting to determine if the same observation could be found, using chromium complexes **2aLi** and **2bLi** as nucleophiles.



(3)

Indeed, when we added aryllithium complexes **2aLi** and **2bLi** to complex **1b**, we succeeded in isolating complexes **3b** and **4b** in 81% and 80% yield, respectively (eq 1). Thus, the presence of one phosphito ligand on the manganese entity enables the addition of aryllithium complexes to the manganese ring to occur and prevents the formation of unstable compounds.

But when complexes **2aLi** and **2bLi** were added to phosphito-disubstituted compound **1c**, the corresponding dinuclear complexes **3c** and **4c** could be isolated in only 52% and 42% yield, respectively (eq 1). The NMR spectroscopic data of these four new complexes **3b**, **3c**, **4b**, and **4c** confirmed the assigned structures. It is interesting to notice the shielding effect (reported in Table 1) of the phosphito ligands, less π-accepting than the CO ligands, on the η^5-cyclohexadienyl protons. Taken as a whole, this shielding effect is weaker for the H9,11 protons than for the H8,12 and H10 protons (Table 1). The same effect was observed for the corresponding ^{13}C NMR signals.

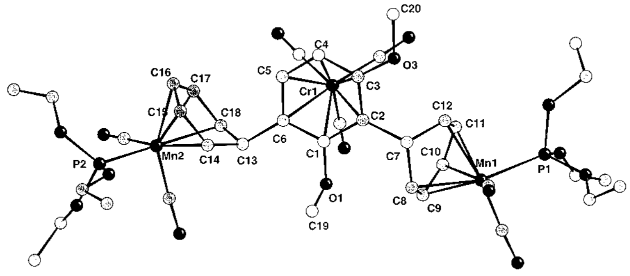
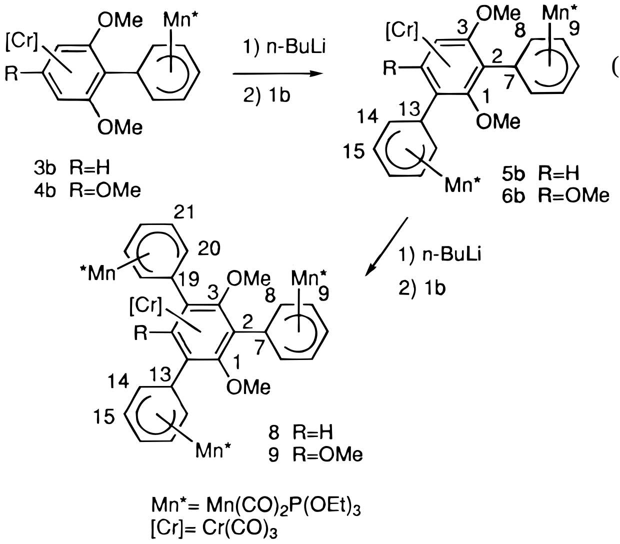


Figure 1. ORTEP diagram of complex **5b**.

It appears that although the role of the phosphito ligand was important, the optimum effect (the best yield) was obtained when only one CO of the manganese complex was substituted by one triethylphosphito ligand. So, all of the following experiments were carried out with the P(OEt)3-monosubstituted manganese compound **1b**.

Trinuclear Complexes. Complexes **3b** and **4b** were subsequently converted into the corresponding aryllithium (after reaction with 1.1 equiv of *n*-BuLi), which added to the manganese complex **1b** to give the trinuclear complexes **5b** and **6b** in 63% and 61% yield, respectively (eq 4).



(4)

X-ray-quality crystals of **5b** were grown from a diethyl ether/pentane mixture at −10 °C. The structure appears in Figure 1, whereas the crystallographic data and the most important bond distances and bond angles can be found in Tables 2 and 3.

Tetranuclear Complexes. In turn, complexes **5b** and **6b** could be lithiated and reacted with complex **1b**, giving "carousel-like" tetranuclear complexes **8** and **9** in 36% and 33% yield respectively (eq 4). The ^{1}H NMR spectra require careful examination concerning the η^5-cyclohexadienyl ring protons, especially the protons β to the sp^3 carbons. We note that for the compounds where one of the η^5-cyclohexadienyl manganese rings straddles the molecular mirror plane (complexes **3b** and **8**, Chart 2), only one signal is observed for the two **a** protons of the A ring (4.77 ppm for **3b**). For the two other η^5-cyclohexadienylmanganese rings (B rings of complex **8**, Chart 2), separate signals are observed for the diastereotopic **b** and **c** protons (4.75 and 5.01 ppm, respectively). The same feature occurs in the A and B

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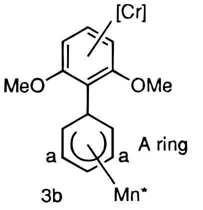
Table 2. Crystal Data for 5b and 9

	5b	**9**
mol formula	$C_{39}H_{48}O_{15}P_2Mn_2Cr$	$C_{54}H_{72}O_{26}P_3Mn_3Cr$
fw	982.6	1366.8
a (Å)	15.792(4)	15.167(3)
b (Å)	17.893(3)	15.858(6)
c (Å)	16.975(2)	26.251(7)
α (deg)	90	90
β (deg)	109.51(1)	90
γ (deg)	90	90
V (Å^3)	4521(1)	6314(3)
Z	4	4
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$Pna2_1$
linear abs coeff μ (cm^{-1})	8.89	8.69
density ρ (g cm^{-3})	1.44	1.44
diffractometer	CAD4 Enraf-Nonius	CAD4 Enraf-Nonius
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
scan type	$\omega/2\theta$	$\omega/2\theta$
scan range (deg)	$0.8 + 0.345 \tan \theta$	$0.8 + 0.345 \tan \theta$
θ limits (deg)	1−25	1−25
temp. of measurement	room temp	room temp
octants collected	0,18; 0,21; −20,19	0,18; 0,18; 0,31
no. of data collected	8542	6132
no. of unique data collected	7935	5664
no. of unique data used for refinement	2810 $(F_o)^2 > 3\sigma(F_o)^2$	2707 $(F_o)^2 > 3\sigma(F_o)^2$
R(int)	0.0195	no
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0671	0.0629
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.0720, w = 1.0	0.0671, w = 1.0
abs corr	no	no
ext param	98	250
no. of variables	473	486
$\Delta\rho$(min) (e Å^{-3})	−0.71	−0.41
$\Delta\rho$(max) (e Å^{-3})	1.74	0.54

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 5b and 9

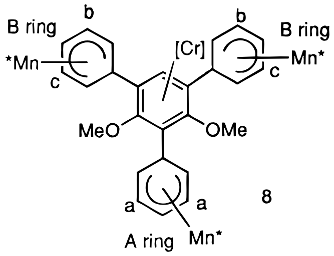
	Complex **5b**		
C6−C13	1.52(2)	C1−Cr−C3	65.9(5)
C2−C7	1.55(2)	C3−Cr−C5	66.0(5)
Mn1−C10	2.14(2)	C5−Cr−C1	67.6(5)
Mn2−C16	2.13(1)		
Mn2−C14	2.21(1)		
Mn2−C18	2.23(2)		
	Complex **9**		
C4−C19	1.52(3)	C5−O5−C27	113.3(15)
C2−C7	1.57(2)	C1−O1−C25	113.3(14)
C6−C13	1.53(3)	C3−O3−C26	113.4(14)
Mn1−C10	2.08(2)		
Mn2−C16	2.11(2)		
Mn3−C23	2.10(3)		

Chart 2



3b

Mn*= Mn(CO)$_2$P(OEt)$_3$
[Cr]= Cr(CO)$_3$



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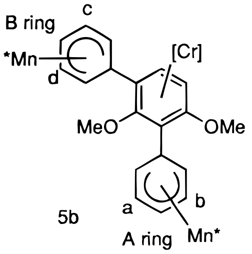
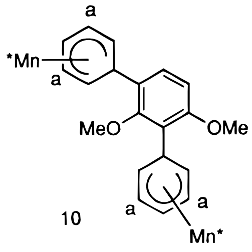


5b



10

rings of complex **5b** (Chart 2): in this case, four distinct signals are observed, as expected, for the two pairs of diastereotopic protons: **a**, **b** and **c**, **d** (4.69, 4.78 and 4.85, 4.92 ppm respectively).

To determine the role of the chromium entity in these NMR features, we were able to selectively decoordinate the chromium entity of complex **5b** by simply exposing a solution of this complex in $CHCl_3$ to sunlight: bimetallic complex **10** (Chart 2), without any planar chirality, was formed. ^{1}H NMR data of this complex show only one multiplet for the four η^5-cyclohexadienyl ring **a** protons (4.72 ppm, Chart 2). These NMR data can be related to the elegant work of Mc Glinchey, Jaouen, et al.[24] who conducted an NMR study of mono-, bis-, and tris-$Cr(CO)_3$ complexes of triphenyl silanol and have observed the same features due to symmetry reasons.

One-Pot Reactions. We succeeded in developing a one-pot procedure to synthesize tetranuclear complexes such as **8** directly from **1b** and **2aLi**. A solution of complex **1b** in THF was added to a solution of 1 equiv of lithiated complex **2aLi**. After 20 min of stirring at room temperature, 1.1 equiv of n-BuLi was added to the mixture at −78 °C. After 1 h of stirring at this temperature, a second solution of 1 equiv of complex **1b** was transferred to the previous mixture. After addition of n-BuLi and complex **1b** for the third time under the same conditions, we isolated trimetallic **5b** and tetrametallic **8** (49% and 45% yield, respectively). The same experiment starting from **1b** and **2b** gave rise to the

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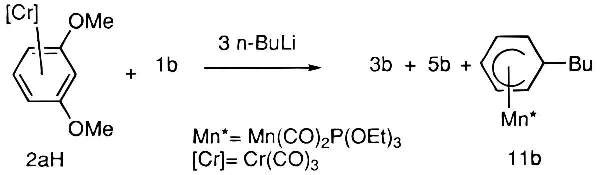
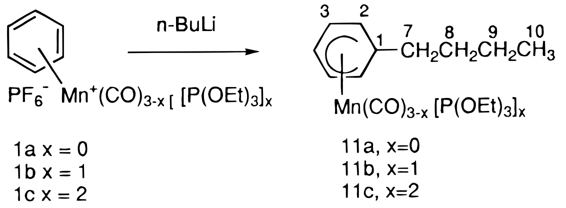
formation of complexes **6b** and **9** in 52% and 46% yield, respectively.

Finally, the addition of 3 equiv of *n*-BuLi directly to a mixture of 3 equiv of **1b** and 1 equiv of **2aH** in THF (eq 5) led to the formation of complexes **3b** (45% yield) and **5b** (8% yield). No evidence for the formation of tetranuclear complex **8** was seen; instead, a novel reaction occurred in which the lithiated base *n*-BuLi was added to the cationic benzenemanganese complex ring to give the η^5-cyclohexadienyl complex **11b** (66% yield calculated from **1b**).



(5)

In these experimental conditions, the role of *n*-BuLi could, thus, be two-fold: it reacted as a base with the neutral chromium complex and as a nucleophile with the cationic manganese complex. This competitive reaction clearly confirms the very high electrophilicity of (η^6-arene)manganese complexes. Indeed, in the absence of the (arene)tricarbonylchromium complex, we showed that *n*-BuLi could react instantaneously at low temperature with complexes **1a**, **1b**, and **1c** as well, giving the corresponding η^5-cyclohexadienyl complexes **11a**, **11b**, and **11c**, respectively, in quantitative yields (eq 6).



(6)

Confirmation of the different modes of coordination of the manganese and chromium atoms to the different rings was provided by the X-ray structure of **9** whose ORTEP drawing is reported Figure 2. Crystal data and selected bond distances and angles are given in Tables 2 and 3.

The ORTEP views shown in Figures 1 and 2 clearly demonstrate the following points: (1) concerning the arene Cr complex structures of **5b** and **9**, the carbons bearing the methoxy groups are eclipsed by chromium–carbonyl bonds.[25] One methoxy group in complex **5b** (at C1) and the three methoxy groups in complex **9** are pointing away from the $Cr(CO)_3$ entity. (2) Concerning the Mn ring structures, they are characteristic of η^5 coordination in both complexes. Indeed, five ring carbon atoms are almost planar, while the remaining atom lies on the opposite side of this plane from the $Mn(CO)_2P(OEt)_3$ moiety. The planes make an angle of 38° with the C7C8C12 plane and an angle of 36° with the C13C14C18 plane (complex **5b**), in the range of values observed for other η^5-cyclohexadienyl complexes.[26] As for complex **9**, it is noteworthy that the corresponding angles are less open: 29°, 31°, and 31° for the angles of the η^5-cyclohexadienyl planes with the C7C8C12 (Mn1 ring), C13C14C18 (Mn2 ring), and C19C20C24 planes, (Mn3 ring), respectively. The presence of the third manganese atom does not seem to affect these η^5-cyclohexadienyl structures.

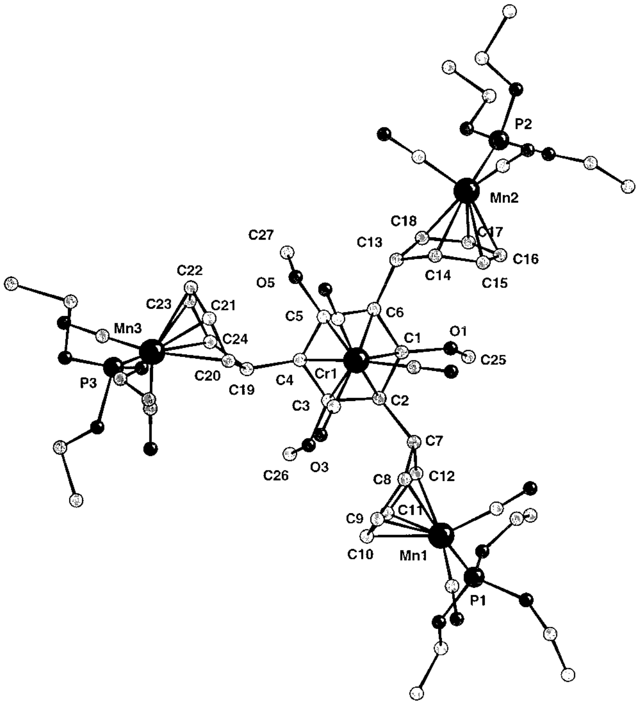


Figure 2. ORTEP diagram of complex **9**.

In summary, by combining the specific properties of cationic (η^6-arene)manganese complexes (high electrophilicity) and of (η^6-arene)chromium complexes (easy and regioselective deprotonation), it was possible to synthesize new hetero di-, tri-, and tetrametallic complexes whose properties are being studied. Further work is in progress in order to apply this method to the synthesis of other polymetallic complexes using, as the starting material, electrophilic complexes of other metals.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere. All experiments were always protected from exposure to light and oxygen. Workup procedures were done in air. Tetrahydrofuran (THF) and di-*n*-butyl ether (DBE) used were distilled over sodium benzophenone ketyl anion under a dry nitrogen atmosphere.

^1H and ^{13}C NMR spectra were obtained with Brücker AC 200 and 400 spectrometers. Infrared spectra were recorded on Perkin-Elmer 1420 and Brücker FT spectrometers. Elemental analyses were performed by Le Service de Microanalyses de l'Université P. et M. Curie. Melting points were measured on a Reichert apparatus.

Synthesis. Preparation of (η^6-Arene)manganese Complexes. (η^6-Benzene)tricarbonylmanganese Hexafluo-

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(25) The conformations of $Cr(CO)_3$ entities can be related to those of other complexes substituted with electron-donating groups, see for example: (a) Saillard, J. Y.; Grandjean, D.; Le Meaux, P.; Jaouen, G.; Top, S.; Decken, A.; McGlinchey, M. J. *Nouv. J. Chim.* **1981**, *5*, 153. (b) Rose-Munch, F.; Bellot, O.; Mignon, L.; Semra, A.; Robert, F.; Jeannin, Y. *J. Organomet. Chem.* **1991**, *402*, 1.

(26) For X-ray structures of η^5-cyclohexadienyl complexes where the Mn atom is substituted by phosphorous ligands, see: (a) Connelly, N. G.; Freemann, M. J.; Orpen, A. G.; Sheehan, A. R.; Sheridan, J. B.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1019. (b) Snyder, D. B.; Schauer, S. J.; Eyman, D. P.; Moler, J. L.; Weers, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 6718.

rophosphate Complex 1a: Yield 92%; lit.[31] 72%. IR (CH_3CN): ν(CO) 2075, 2035, 2010 cm^{-1}. ^{1}H NMR ($(CD_3)_2CO$): δ 6.88, s. ^{13}C NMR ($(CD_3)_2CO$): δ 216.3 ($Mn(CO)_3$), 102.5 (CH).

Complexes 1b and 1c. In a typical procedure,[26b,32] cationic complex **1a** (500 mg, 1.38 mmol) was dissolved in freshly distilled acetone (50 mL). $P(OEt)_3$ (470 μL, 2.74 mmol) and then Me_3NO (a pinch) were added and mixed at room temperature for 3 h. Solvents were removed under reduced pressure. The crude oil was chromatographed on silica gel (60 μ) (($(CH_3)_2CO:CH_2Cl_2$) to give **1b** (1.07 mmol, 77% yield, lit.[26b] 88%).

Complex 1c: Mp 132 °C (dec). Yield 54% from **1b.** Anal. Calcd for $C_{19}H_{36}MnO_7P_3F_6$: C, 35.75; H, 5.68. Found: C, 35.95; H, 5.71. IR: ν(CO) 1940 cm^{-1}. ^{1}H NMR (400 MHz, $(CD_3)_2CO$, ppm): δ 5.90 (t, $J = 2.1$ Hz), 4.15 (m, $P(OCH_2CH_3)_3$), 1.34 (t, $J = 7.1$ Hz, $P(OCH_2CH_3)_3$). ^{13}C NMR, $(CD_3)_2CO$, ppm): δ 226.2 (t, $J = 45.5$ Hz, Mn−CO), 94.6 (C_6H_6), 63.1 ($P(OCH_2CH_3)_3$), 16.1 ($P(OCH_2CH_3)_3$). ^{31}P NMR (162 MHz, $(CD_3)_2CO$, ppm): δ 181.5.

Preparation of (η^6-Arene)chromiumtricarbonyl Complexes. Complexes **2aH** and **2bH** were synthesized according to literature methods. Yields: 90% of **2aH** (lit.[33] 45%), 90% of **2bH** (lit.[33] 5%).

Preparation of Complexes 3−6, 8, and 9. Typical procedure: to a solution of complex **2aH** (274 mg, 1.0 mmol) in THF was added a hexane solution of *n*-BuLi (1.5 M, 0.73 mL, 1.1 mmol) at −78 °C. The resulting solution was stirred for 1 h at −78 °C and then added, through a cannula, to a solution of complex **1a** (434 mg, 1.2 mmol) in 15 mL of THF at −78 °C. Immediately after this addition, distilled water (20 mL) and then Et_2O (30 mL) were added. The mixture was warmed and extracted at room temperature with Et_2O. The organic phase was washed with brine, dried over $MgSO_4$, and filtered through a Celite column. Solvents were removed under a nitrogen flush at low temperature. The yellow oil was purified by flash chromatography on silica gel (15−40 μ) to give the starting complex (η^6-dimethoxy-1,3 benzene)$Cr(CO)_3$ (**2aH**; 54 mg, 0.2 mmol) (Et_2O:PE = 30:100) and bimetallic complex **3a** (Et_2O:PE = 40:100) as a yellow solid (390 mg, 0.8 mmol, 80% yield).

Complex 3a: Mp 139 °C (dec). Anal. Calcd for $C_{20}H_{15}CrMnO_8$: C, 49.00; H, 3.08. Found: C, 48.80; H, 3.07. IR ($CHCl_3$, cm^{-1}): ν(CO) 1875, 1920, 1955, 2005. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.82 (tt, H10, $J = 5.3$ and 1.1 Hz), 5.57 (t, H5, $J = 6.7$ Hz), 5.02 (t, H9 and H11, $J = 5.7$ Hz), 4.62 (d, H4 and H6, $J = 6.7$ Hz), 4.36 (t, H7, $J = 5.7$ Hz), 3.73 (s, 2OMe), 3.47 (m, H8 and H12). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 233.7 (Cr−CO), 223.2 (Mn−CO), 143.8 (C1 and C3), 97.6 (C9 and C11), 97.1 (C2), 92.2 (C5), 78.6 (C10), 68.5 (C4 and C6), 59.9 (C8 and C12), 55.6 (OMe), 31.5 (C7).

Complex 3b: Mp = 112 °C (dec). Yield: 81%. Anal. Calcd for $C_{25}H_{30}CrMnO_{10}P$: C, 47.78; H, 4.81. Found: C,47.60; H, 4.91. IR ($CHCl_3$, cm^{-1}): ν(CO) 1865, 1935, 1955. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 5.49 (t, H5, $J = 6.8$ Hz), 5.49 (m, H10), 4.77 (m, H9 and H11), 4.57 (d, H4 and H6, $J = 6.8$ Hz), 4.37 (t, H7, $J = 6.0$ Hz), 3.94 (m, $P(OCH_2CH_3)_3$), 3.67 (s, 2OMe), 3.11 (t, H8 and H12, $J = 6.0$ Hz), 1.26 (t, $P(OCH_2CH_3)_3$, $J = 7.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 234.0 (Cr−CO), 229.1 (d, Mn−CO, $J = 30.2$ Hz), 144.0 (C1 and C3), 98.5 (C2), 96.4 (C9 and C11), 92.1 (C5), 76.5 (C10), 68.7 (C4 and C6), 60.2 ($P(OCH_2CH_3)_3$), 57.0 (OMe), 55.5 (C8 and C12), 37.7 (C7), 16.3 ($P(OCH_2CH_3)_3$). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 197.6 ($P(OCH_2CH_3)_3$).

Complex 3c: Mp 155 °C (dec). Yield: 52%. Anal. Calcd for $C_{30}H_{45}CrMnO_{12}P_2$: C, 47.01; H, 5.92. Found: C, 47.13; H, 5.95. IR ($CHCl_3$, cm^{-1}): 1960, 1875. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.44 (t, $J = 6.8$ Hz, H5), 5.15 (m, H10), 4.64 (t, $J = 5.7$ Hz, H9 and H11), 4.56 (d, $J = 6.8$ Hz, H4 and H6), 4.43 (t, $J = 5.7$ Hz, H7), 3.99 (m, $P(OCH_2CH_3)_3$), 3.66 (s, CH_3 at C1 and C3), 2.70 (m, H8 and H12), 1.25 (t, $J = 7.0$ Hz, $P(OCH_2CH_3)_3$). ^{13}C NMR (50 MHz, $CDCl_3$): 234.3 (CO(Cr)), 229.9 (t, $J = 35.1$ Hz, CO(Mn)), 144.1 (C1 and C3), 99.8 (C2), 94.6 (C9 and C11), 91.8 (C5), 74.5 (C10), 68.9 (C4 and C6), 59.5 ($P(OCH_2CH_3)_3$), 55.3 (CH_3 at C1 and C3), 53.9 (C8 and C12), 31.4 (C7), 16.4 ($P(OCH_2CH_3)_3$). ^{31}P NMR (162 MHz, $CDCl_3$): 190.2.

Complex 4a: Mp 183 °C (dec). Yield: 42%. Anal. Calcd for $C_{21}H_{17}MnCrO_3$: C, 48.48; H, 3.29. Found: C, 48.54; H, 3.35. IR ($CHCl_3$, cm^{-1}): ν(CO) 1855, 1865, 1935 (Cr), 1955, 2015 (Mn). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 5.76 (tt, H10, $J = 6.0$ and 1.3 Hz), 4.95 (t, H9 and H11, $J = 6.0$ Hz), 4.71 (s, H4 and H6), 4.24 (t, H7, $J = 6.0$ Hz), 3.76 (s, OCH_3 at C1 and C3), 3.72 (s, OCH_3 at C5), 3.42 (t, H8 and H12, $J = 6.0$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 234.1 (Cr−CO), 223.4 (Mn−CO), 142.4 (C1 and C3), 141.3 (C5), 97.7 (C9 and C11), 93.3 (C2), 78.6 (C10), 60.2 (C4 and C6), 60.0 (C8 and C12), 55.9 (OCH_3 at C5), 55.8 (OCH_3 at C1 and C3), 31.2 (C7).

Complex 4b: Mp 144 °C (dec). Yield: 41%. Anal. Calcd for $C_{26}H_{32}CrMnO_{12}P$: C, 47.43; H, 4.90. Found: C, 47.41; H, 4.90. IR ($CHCl_3$, cm^{-1}): ν(CO) 1860, 1940. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 5.49 (t, H10, $J = 6.0$ Hz), 4.79 (t, H9 and H11, $J = 6.0$ Hz), 4.70 (s, H4 and H6), 4.30 (t, H7, $J = 6.0$ Hz), 3.94 (m, $P(OCH_2CH_3)_3$), 3.71 (s, OCH_3 at C1, C3), 3.66 (s, OCH_3 at C5), 3.07 (t, H8 and H12, $J = 6.0$ Hz), 1.27 (t, $P(OCH_2CH_3)_3$, $J = 7$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 234.5 (Cr−CO), 229.1 (d, Mn−CO, $J = 32.0$ Hz), 142.8 (C1 and C3), 141.4 (C5), 96.8 (C9 and C11), 94.8 (C2), 77.7 (C10), 60.6 ($P(OCH_2CH_3)_3$), C4 and C6), 57.4 (C8 and C12), 56.0 (OCH_3 at C5), 55.8 (OCH_3 at C1 and C3), 31.6 (C7), 16.7 ($P(OCH_2CH_3)_3$). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 197.6 ($P(OCH_2CH_3)_3$).

Complex 4c: Mp 151 °C (dec). Yield: 42%. Anal. Calcd for $C_{31}H_{47}CrMnO_{13}P_2$: C, 46.74; H, 5.92. Found: C, 46.92; H, 5.94. IR ($CHCl_3$, cm^{-1}): 1950, 1860. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.16 (m, H10), 4.72 (s, H4 and H6), 4.65 (t, $J = 5.7$ Hz, H9 and H11), 4.36 (t, $J = 5.7$ Hz, H7), 4.01 (m, $P(OCH_2CH_3)_3$), 3.86 (s, CH_3 at C1 and C3), 3.80 (s, CH_3 at C5), 2.68 (m, H8 and H12), 1.29 (t, $J = 6.9$ Hz, $P(OCH_2CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 234.6 (CO(Cr)), 230.7 (CO-(Mn)), 143.1 (C1 and C3), 141.3 (C5), 96.1 (C2), 95.0 (C9 and C11), 74.8 (C10), 60.8 (C4 and C6), 59.9 ($P(OCH_2CH_3)_3$), 56.2 (CH_3 at C1 and C3), 55.7 (CH_3 at C5), 54.4 (C8 and C12), 31.3 (C7), 16.8 ($P(OCH_2CH_3)_3$).

Complex 5b: Mp 162 °C (dec). Anal. Calcd for $C_{39}H_{50}CrMn_2O_{15}P_2$: C, 47.67; H, 5.13. Found: C,47.61; H, 5.33. IR ($CHCl_3$, cm^{-1}): ν(CO) 1960, 1945, 1875. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.53 (m, H10 and H16), 5.31 (d, H5, $J = 7.0$ Hz), 4.92 (m, H15 or H17), 4.85 (m, H17 or H15), 4.78 (t, H9 or H11, $J = 5.6$ Hz), 4.69 (t, H11 or H9, $J = 5.6$ Hz), 4.45 (d, H4, $J = 7.0$ Hz), 4.23 (t, H7, $J = 5.6$ Hz), 3.97 (m, $P(OCH_2CH_3)_3$), 3.77 (s, OCH_3 at C1), 3.66 (t, H13, $J = 5.6$ Hz), 3.63 (s, OCH_3 at C3), 3.10 (m, H8, H12 and H14 or H18), 3.01 (t, H14 or H18, $J = 5.6$ Hz), 1.30 (m, $P(OCH_2CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 233.8 (Cr−CO), 229.2 (d, Mn−CO, $J = 34.4$ Hz), 228.5 (d, Mn−CO, $J = 28.3$ Hz), 143.1 (C1), 141.4 (C3), 105.8 (C6), 100.7 (C2), 96.6, 96.3, 95.4, 94.5 (C17, C15, C11, C9), 93.0 (C5), 77.9 and 77.3 (C10 and C6), 69.3 (C4), 64.0 (OCH_3 at C1), 60.3 and 60.5 ($P(OCH_2CH_3)_3$), 57.6, 57.2,

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56.0, and 55.8 (C18, C14, C12, and C8), 55.0 (OCH_3 at C3), 32.2 (C7), 31.9 (C13), 16.4 ($P(OCH_2\mathit{C}H_3)_3$). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ 197.4 and 196.0 ($P(OCH_2CH_3)_3$).

Complex 6b: Mp 186 °C (dec). Anal. Calcd for $C_{40}H_{52}CrMn_2O_{16}P_2$: C, 47.44; H, 5.18. Found: C, 47.39; H, 5.20. IR ($CHCl_3$, cm^{-1}): ν(CO) 1950, 1935, 1870. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.32 (m, H10 and H16), 4.84 (m, H9 and H15 or H11 and H17), 4.76 (t, H9 and H15 or H11 and H17, $J = 6.2$ Hz), 4.48 (s, H4), 4.14 (t, H7 and H13, $J = 5.6$ Hz), 4.00 (m, $P(OC\mathit{H}_2CH_3)_3$), 3.74 (s, OCH_3 at C1), 3.70 (s, OCH_3 at C3 and C5), 3.05 (m, H8, H12, H14, and H18), 1.30 (m, $P(OCH_2C\mathit{H}_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 234.1 (Cr−CO), 229.4 (d, Mn−CO, $J = 33.0$ Hz), 228.5 (d, Mn−CO, $J = 32.0$ Hz), 142.4 (C1), 141.4 (C3 and C5), 96.6 (C9 and C15 or C11 and C17), 96.4 (C2 and C6), 96.3 (C9 and C15 or C11 and C17), 76.8 (C10 and C16), 63.9 (OCH_3 at C1), 60.3 ($P(O\mathit{C}H_2CH_3)_3$), 58.1 (C8 and C14 or C12 and C18), 57.6 (C4), 57.3 (C8 and C14 or C12 and C18), 54.8 (OCH_3 at C3 and C5), 31.8 (C7 and C13), 16.4 ($P(OCH_2\mathit{C}H_3)_3$). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 197.6 ($P(OCH_2CH_3)_3$).

Complex 8: Mp 175 °C (dec). Anal. Calcd for $C_{53}H_{70}CrMn_3O_{20}P_3$: C, 47.62; H, 5.28. Found: C, 47.37; H, 5.30. IR ($CHCl_3$, cm^{-1}): ν(CO) 1960, 1940, 1875. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.69 (m, H16 and H22), 5.56 (m, H10), 5.20 (s, H5), 5.01 (m, H15 and H23 or H17 and H21), 4.84 (m, H9 and H11), 4.75 (H17 and H21 or H15 and H23), 4.11 (t, H7, $J = 5.5$ Hz), 3.98 (m, $P(OC\mathit{H}_2CH_3)_3$), 3.71 (s, OCH_3 at C1 and C3), 3.57 (t, H13 and H19, $J = 5.3$ Hz), 3.13 (m, H8, H12 and H14 and H24 or H18 and H20), 2.97 (m, H18 and H20 or H14 and H24), 1.31 (m, $P(OCH_2C\mathit{H}_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 233.8 (Cr−CO), 228.6 (m, Mn−CO), 140.2 (C1 and C3), 107.0 (C4 and C6), 103.0 (C2), 96.1 (C9 and C11), 95.4 (C15 and C23 or C17 and C21), 94.5 (C17 and C21 or C15 and C23), 94.1 (C5), 78.0 (C10), 76.8 (C16 and C22), 64.1 (OCH_3 at C1 and C3), 60.4 and 60.6 ($P(O\mathit{C}H_2CH_3)_3$), 57.8 (C14 and C24 or C18 and C20), 55.7 (C18 and C20 or C14 and C24), 32.8 (C13 and C19), 32.0 (C7), 16.4 and 16.5 ($P(OCH_2\mathit{C}H_3)_3$). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 195.9 and 197.1 ($P(OCH_2CH_3)_3$).

Complex 9: Mp 158 °C (dec). Anal. Calcd for $C_{54}H_{72}CrMn_3O_{21}P_3$: C, 47.45; H, 5.31. Found: C, 47, 46; H, 5.31. IR ($CHCl_3$, cm^{-1}): ν(CO) 1960, 1935, 1870. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.55 (m, H10, H16, and H22), 4.84 (m, H9, H11, H15, H17, H21, and H23), 3.97 (m, H7, H13, H19, and $P(OC\mathit{H}_2CH_3)_3$), 3.64 (s, OCH_3 at C1, C3, and C5), 3.10 (t, H8, H12, H14, H18, H20, and H24, $J = 6.1$ Hz), 1.30 (m, $P(OCH_2C\mathit{H}_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 234.6 (Cr−CO), 229.0 (d, Mn−CO, $J = 32.0$ Hz), 143.4 (C1, C3, and C5), 100.4 (C2, C4, and C6), 96.0 (C9, C11, C15, C17, C21, and C23), 78.2 (C10, C16, and C22), 63.2 (C8, C12, C14, C18, C20, and C24), 60.3 ($P(O\mathit{C}H_2CH_3)_3$), 57.5 (OCH_3 at C1, C3, and C5), 32.3 (C7, C13, and C19), 16.4 ($P(OCH_2\mathit{C}H_3)_3$). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 197.3 ($P(OCH_2CH_3)_3$).

Complex 10: Mp 140 °C (dec). Yield: 75%. Anal. Calcd for $C_{36}H_{50}Mn_2O_{12}P_2$: C, 51.07; H, 5.95. Found: C, 49.55; H, 5.81. IR ($CHCl_3$, cm^{-1}): ν(CO) 1940, 1870. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 6.81 (d, H5, $J = 8.6$ Hz), 6.46 (d, H4, $J = 8.6$ Hz), 5.54 (m, H10 or H16), 5.48 (m, H16 or H10), 4.72 (m, H9, H11, H15, and H17), 4.51 (t, H7, $J = 5.6$ Hz), 4.05 (t, H13, $J = 5.7$ Hz), 3.98 (m, $P(OC\mathit{H}_2CH_3)_3$), 3.73 (s, OCH_3 at C1 or C3), 3.71 (s, OCH_3 at C3 or C1), 3.19 (m, H8, H12, H14, and H18), 1.31 (m, $P(OCH_2C\mathit{H}_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 228.8 (d, Mn−CO, $J = 34.4$ Hz), 228.2 (d, Mn−CO, $J = 32.4$ Hz), 156.7 (C1), 152.9 (C3), 133.1 (C6), 125.9 (C5), 105.6 (C4), 103.6 (C2), 94.9 (C9 and C11 or C15 and C17), 94.1 (C15 and C17 or C9 and C11), 76.8 (C10 or C16), 76.5 (C16 or C10), 61.7 (OCH_3 at C1), 59.2 and 59.0 ($P(O\mathit{C}H_2CH_3)_3$), 55.9 (C8 and C12 or C14 and C18), 55.2 (C14 and C18 or C8 and C12), 54.1 (OCH_3 at C3), 32.2 (C7), 31.6 (C13), 15.3 and 15.2 ($P(OCH_2\mathit{C}H_3)_3$). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 198.2 and 197.3.

Preparation of Complexes 7 and 11. Typical Procedure: To a solution of complex **1a** (362 mg, 1.0 mmol) in THF (15 mL) was added an Et_2O solution of mesityllithium (1.3 mmol). The resulting solution was stirred for 15 min at −78 °C then for 10 min at room temperature. Et_2O (30 mL) and distilled water (20 mL) were added to the solution. The aqueous phase was extracted with Et_2O (30 mL). The organic phase was washed with brine, dried over $MgSO_4$, and filtered through a Celite column. Solvents were removed under a nitrogen flush at low temperature. The red oil (308 mg) was purified by flash chromatography on silica gel (20 μ) to give complex **7a** (Et_2O: PE = 3:1) as a yellow solid (127 mg, 0.38 mmol, 38% yield).

Complex 7a: Mp 129 °C (dec). Yield: 38%. Anal. Calcd for $C_{18}H_{17}MnO_3$: C, 64.30; H, 5.10. Found: C, 64.10; H, 5.07. IR ($CHCl_3$, cm^{-1}): ν(CO) 1995, 1910. ^1H NMR (200 MHz, $CDCl_3$, ppm): δ 6.76 (s, H4 and H6), 5.85 (tt, $J = 6.0$ and 1.0 Hz, H10), 5.03 (td, $J = 6.0$ and 1.0 Hz, H9 and H11), 4.68 (t, $J = 6.0$ Hz, H7), 3.58 (td, $J = 6.0$ and 1.0 Hz, H8 and H12), 2.42 (s, $2CH_3$ at C1 and C3), 2.22 (s, CH_3 at C5). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 226.1 (CO), 139.6 (C5), 136.3 (C2), 135.6 (C1 and C3), 130.9 (C4 and C6), 98.7 (C9 and C11), 77.2 (C10), 62.9 (C8 and C12), 37.3 (C7), 22.9 (CH_3 at C1 and C3), 20.6 (CH_3 at C5).

Complex 7b: Mp 132 °C (dec). Yield: 54%. Anal. Calcd for $C_{23}H_{32}MnO_5P$: C, 58.23; H, 6.80. Found: C, 58.13; H, 6.83. IR ($CHCl_3$, cm^{-1}): ν(CO) 1935, 1870. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 6.79 (s, H4 and H6), 5.66 (m, H10), 4.90 (m, H9 and H11), 4.79 (t, $J = 5.6$ Hz, H7), 4.08 (m, $P(OC\mathit{H}_2CH_3)_3$), 3.33 (t, $J = 6.2$ Hz, H8 and H12), 2.50 (s, CH_3 at C1 and C3), 2.27 (s, CH_3 at C5), 1.39 (t, $J = 7.0$ Hz, $P(OCH_2C\mathit{H}_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 228.1 (d, $J = 34.4$ Hz, CO), 139.4 (C5), 134.5 (C1, C2, C3), 129.6 (C4, C6), 96.4 (C9, C11), 79.1 (C10), 59.2 ($P(O\mathit{C}H_2CH_3)_3$), 58.6 (C8, C12), 36.2 (C7), 21.7 (CH_3 at C1 and C3), 19.5 (CH_3 at C5), 15.3 ($P(OCH_2\mathit{C}H_3)_3$). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 197.5.

Complex 7c: Mp 140 °C (dec). Yield: 74%. Anal. Calcd for $C_{28}H_{47}MnO_7P_2$: C, 54.90; H, 7.73. Found: C, 56.02; H, 7.81. IR ($CHCl_3$, cm^{-1}): ν(CO) 1855. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 6.80 (s, H4 and H6), 5.37 (m, H10), 4.83 (H7, H9, and H11), 4.19 (m, $P(OC\mathit{H}_2CH_3)_3$), 2.97 (m, H8 and H12), 2.57 (s, CH_3 at C1 and C3), 2.30 (s, CH_3 at C5), 1.43 (t, $J = 7.0$ MHz, $P(OCH_2C\mathit{H}_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 230.1 (t, $J = 35.0$ Hz, CO), 140.5 (C5), 134.6 (C1, C2, and C3), 129.4 (C4 and C6), 94.6 (C9 and C11), 72.5 (C10), 58.5 ($P(O\mathit{C}H_2CH_3)_3$), 55.4 (C8 and C12), 35.6 (C7), 21.8 (CH_3 at C1 and C3), 19.4 (CH_3 at C5), 15.4 ($P(OCH_2\mathit{C}H_3)_3$). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 199.1.

Complex 11a: Mp 145 °C (dec). Yield: 80%. Anal. Calcd for $C_{13}H_{15}MnO_3$: C, 56.94; H, 5.51. Found: C, 56.89; H, 5.55. IR (CCl_4, cm^{-1}): ν(CO) 2005, 1935. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.69 (t, $J = 6.2$ Hz, H4), 4.70 (t, $J = 6.2$ Hz, H3 and H5), 3.14 (t, $J = 6.2$ Hz, H2 and H6), 2.38 (m, H1), 1.07 (m, CH_2 at C9), 0.95 (q, $J = 6.8$ Hz, CH_2 at C8), 0.74 (t, $J = 7.2$ Hz, CH_3 at C10), 0.62 (m, CH_2 at C7). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 223.3 (CO), 96.0 (C3 and C5), 79.7 (C4), 57.9 (C2 and C6), 42.4 (CH_2 at C7), 35.0 (C1), 26.4 (CH_2 at C8), 22.5 (CH_2 at C9), 14.0 (CH_3 at C10).

Complex 11b: Mp 151 °C (dec). Yield: 89%. Anal. Calcd for $C_{18}H_{30}MnO_5P_1$: C, 52.43; H, 7.33. Found: C, 52.28; H, 7.42. IR ($CHCl_3$, cm^{-1}): ν(CO) 1935, 1865. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.50 (m, H4), 4.57 (m, H3 and H5), 3.96 (m, $P(OC\mathit{H}_2CH_3)_3$), 2.94 (t, $J = 6.2$ Hz, H2 and H6), 2.44 (m, H1), 1.27 (t, $J = 7.1$ Hz, $P(OCH_2C\mathit{H}_3)_3$), 1.14 (m, CH_2 at C9), 1.04 (q, $J = 5.3$ Hz, CH_2 at C8), 0.82 (t, $J = 7.2$ Hz, CH_3 at C10), 0.62 (m, CH_2 at C7). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 229.8 (d, $J = 33.0$ Hz, CO), 94.5 (C3 and C5), 78.7 (C4), 60.1 ($P(O\mathit{C}H_2CH_3)_3$), 54.9 (C2 and C6), 42.3 (CH_2 at C7), 35.1 (C1), 26.5 (CH_2 at C8), 22.6 (CH_2 at C9), 16.4 ($P(OCH_2\mathit{C}H_3)_3$), 14.1 (CH_3 at C10). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 197.6.

Complex 11c: Mp 152 °C (dec). Yield: 82%. Anal. Calcd for $C_{23}H_{45}MnO_7P_2$: C, 50.18; H, 8.24. Found: C, 50.10; H, 8.25. IR ($CHCl_3$, cm^{-1}): ν(CO) 1840. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.19 (m, H4), 4.43 (m, H3 and H5), 3.97 (m, $P(OCH_2CH_3)_3$), 2.51 (m, H2 and H6), 2.35 (m, H1), 1.25 (t, $J = 7.1$ Hz, $P(OCH_2CH_3)_3$), 1.11 (m, CH_2 at C9), 0.98 (q, $J = 5.3$ Hz, CH_2 at C8), 0.79 (t, $J = 7.2$ Hz, CH_3 at C10), 0.54 (m, CH_2 at C7). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 230.5 (t, $J = 35.0$ Hz, CO), 92.7 (C3 and C5), 75.8 (C4), 59.5 ($P(OCH_2CH_3)_3$), 51.9 (C2 and C6), 42.3 (CH_2 at C7), 34.3 (C1), 26.6 (CH_2 at C8), 22.7 (CH_2 at C9), 16.5 ($P(OCH_2CH_3)_3$), 14.2 (CH_3 at C10). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ 198.5.

X-ray Structure Determinations of 5b and 9. For complex **5b**, the selected crystal was a thick plate (0.03 × 0.40 × 0.59 mm), and for complex **9**, the crystal was a little prism (0.18 × 0.20 × 0.52 mm). For both crystals, accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collections (decay <5%). Complete crystallographic data and collection parameters are listed in Table 1. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[28] Scattering factors and corrections for anomalous scattering were taken from ref 29. The structure was solved by direct methods (SHELXS-86[29]) and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms except for the carbon atoms of the ethyl groups. For compound **5b**, these carbon atoms (C(21)−C(32)) showed large displacement parameters and were left isotropic. For compound **9**, only the Cr, Mn, P, and C(1)−C(24) atoms were anisotropically refined, because there were more atoms to refine and less data. Hydrogen atoms were introduced in the last refinements in calculated positions except on the ethyl groups.

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Supporting Information Available: Tables of full bond distances and bond angles, anisotropic thermal parameters and hydrogen atom coordinates for **5b** and **9** (14 pages). Ordering information is given on any current masthead page.

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