Reactivity of Metallophosphide Anions with Electrophilic (Arene)tricarbonylmetal Complexes

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Reaction of metallophosphide anions $[(CO)_xM'PPh_2]^-$ (M′ = Cr, Fe) with neutral tricarbonyl(η^6-fluoroarene)chromium and cationic (η^6-arene)tricarbonylmanganese complexes give rise to the formation of dinuclear complexes. These complexes are obtained either by substitution of the fluoride anion in the (arene)chromium complexes, or by addition to the ring in the (arene)manganese complexes. The X-ray structure of one homodimetallic (Cr–Cr) complex was obtained and compared with its solution structure.

Introduction

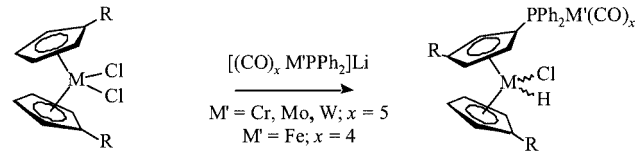
Arenes coordinated to electrophilic neutral $Cr(CO)_3$ or cationic $Mn(CO)_3$ groups undergo a large variety of transformations that would otherwise not be feasible with the free arenes.[1] Among them, nucleophilic additions, followed by acidic and (or) oxidative treatment, provide efficient access to functionalized arenes or cyclohexadienes.[1,2] A wide range of carbon nucleophiles have been shown to react with (η^6-arene)tricarbonylchromium and -manganese complexes,[1] but relatively few investigations have been carried out using organometallic derivatives as the nucleophiles.

In the Mn series, benzylic and homobenzylic organometallic carbanions have been used as nucleophiles. Beck et al., for example, described the reactivity of Mn complexes with deprotonated diphenylmethane or benzothiophene coordinated to $Cr(CO)_3$,[3] as well as with carbonylosmate,[4] carbonylrhenate[5] and anionic alkynyl complexes.[6] More recently, Sweigart et al.[7] demonstrated that a weak nucleophile such as $[Pt(PPh_3)_2(C_2H_4)]$ could cleave a strained C−C bond in the four-membered ring of biphenylene coordinated to an $Mn(CO)_3^+$ fragment, giving the insertion product. Similarly, metal insertion into the C−S and C−O bonds of benzothiophene and benzofuran, respectively, was also observed [the carbocyclic rings of the benzothiophene and the benzofuran were coordinated to $Mn(CO)_3^+$ entities].[8] Metal insertion into the C−Cl bond of cationic tricarbonyl(chloroarene)manganese complexes was also seen.[9a]

Our own contribution in this field has been aimed at studying the reactivity of Fischer-type carbene anions[10] and of deprotonated (alkoxy-substituted arene)tricarbonylchromium complexes[11] towards (η^6-arene)tricarbonylmanganese complexes. These reactions result in the formation of heterodi- or -polymetallic complexes.

In the Cr series, strongly nucleophilic organometallic anions [such as $Fe(CO)_4^{2-}$, $M(CO)_5^{2-}$, M = Cr, W, $CpFe(CO)_2^-$] reacted with $[(C_6H_5X)Cr(CO)_3]$, allowing the formation of dinuclear complexes, which arise as a result of halogen substitution by the organometallic anions.[12]

This has led us to investigate the reaction of metallophosphide anions with (η^6-arene)metal complexes, and for this purpose we have selected the $[(CO)_xM'PPh_2]^-$ anions. These metallophosphide anions are, for example, able to achieve Cp substitution in neutral molybdenocene and tungstenocene dichlorides.[13] The presence of *tert*-butyl or trimethylsilyl groups on the cyclopentadienyl rings does not affect the site of substitution, and products with 1,3-disubstituted Cp-ring[13d] (Scheme 1) are obtained.



R = H, CMe_3, $SiMe_3$
M = Mo, W

Scheme 1. Reaction of metallophosphide anions with metallocene dichlorides

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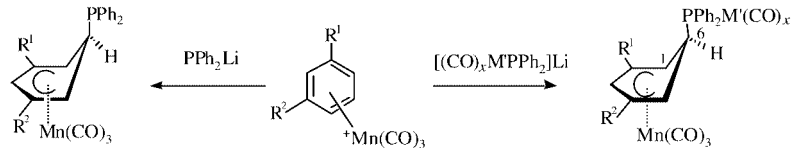


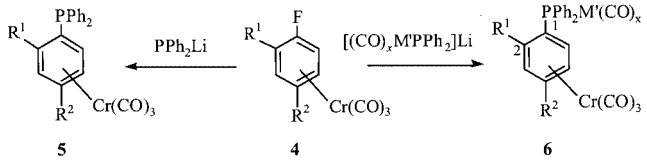
2 1 3

	1a	1b	1c	2a	3aCr]	3a[Fe]	3b[Cr]	3b[Fe]	3c[Cr]
R^1	H	OCH_3	OCH_3	H	H	H	OCH_3	OCH_3	OCH_3
R^2	H	H	OCH_3	H	H	H	H	H	OCH_3
M'					Cr	Fe	Cr	Fe	Cr
x					5	4	5	4	5

Scheme 2. Reaction of metallophosphide anions with $(\eta^6\text{-arene})Mn(CO)_3^+$ complexes

This unexpected reactivity led us to believe that metallophosphide anions are rather good nucleophiles.

In this paper, we describe the reactivity of two metallophosphide anions towards several substituted (η^6-arene)manganese and -chromium complexes (complexes **1**, Scheme 2; and **4**, Scheme 3). The conformational study of one of the resulting dinuclear complexes in the solid state and in solution is also presented.



5 4 6

	4a	4b	4c	5a	5b	5c	6a[Cr]	6b[Cr]	6b[Fe]	6c[Cr]	6c[Fe]
R^1	H	CH_3	H	H	CH_3	H	H	CH_3	CH_3	H	H
R^2	H	H	CH_3	H	H	CH_3	H	H	H	CH_3	CH_3
M'							Cr	Cr	Fe	Cr	Fe
x							5	5	4	5	4

Scheme 3. Reaction of metallophosphide anions with (η^6-arene)-$Cr(CO)_3$ complexes

Results and Discussion

The starting (arene)tricarbonylmanganese (**1a**−**c**) and -chromium (**4a**−**c**) complexes were prepared according to literature procedures.[14,15]

Reactivity towards $[(\eta^6\text{-Arene})Mn(CO)_3]^+$ Complexes

In a preliminary experiment, treatment of a suspension of $[(\eta^6\text{-}C_6H_6)Mn(CO)_3](PF_6)$ (**1a**) in THF with PPh_2Li[16] at −80 °C resulted in the formation of the addition product, the η^5-cyclohexadienyl complex **2a**[17] in a 40% yield, according to Scheme 2.

It is worth noting that when PPh_2Li was added to bent metallocenes $[(\eta^5\text{-}C_5H_5)_2MCl_2]$ (M = Mo, W), the complexity of the reaction mixture did not permit isolation of the desired product.[18a] Similarly, treatment of complex **1a** with $[(CO)_xM'PPh_2]Li$ afforded the neutral complexes **3a[Cr]** and **3a[Fe]** in 55 and 35% yields, respectively. If the reaction was performed with anisole and the 1,3-dimethoxybenzene complexes, **1b** and **1c**, dimetallic derivatives **3b[Cr]**, **3b[Fe]** and **3c[Cr]**[18b] were recovered in 55, 55 and 65% yields, respectively (Scheme 2). It is important to emphasize the *meta* regioselectivity[19] of the nucleophilic addition with respect to the methoxy group in the cases of **1b** and **1c**.

The ^{1}H NMR spectra of the resulting neutral addition complexes (Table 1) features the characteristic signals for the η^5-cyclohexadienyl groups, the 1-H and 5-H protons display low-frequency resonances (between δ = 3.00 and 3.57 ppm), the 2-H and 4-H protons show resonances at almost the same frequency (δ = 4.85−5.07 ppm), and the 3-H protons give signals at the highest frequency (δ = 5.04−5.47 ppm) for the dinuclear complexes **3a[Cr]**, **3a[Fe]**, **3b[Cr]**, **3b[Fe]**, and **3c[Cr]** (Entries 2−6, Table 1), and at

Table 1. ^{1}H NMR spectroscopic data of 6-substituted tricarbonyl[(η^5-1,2,3,4,5)-cyclohexadienyl]manganese complexes

Entry	Complex[a]	1-H, 5-H	2,4-H	3-H	6-H	Ph
1	**2a**	3.16[b] (dd)	5.04[b] (dd)	6.06[b] (t)	3.73 (m)	7.36 (m)
2	**3a[Cr]**	3.56[b] (dd)	4.85[b] (dd)	5.18[b] (t)	4.30[c] (td)	7.54 (m)
3	**3a[Fe]**	3.57[b] (dd)	4.99[b] (dd)	5.47[b] (t)	4.36 (m)	7.59 (m)
4	**3b[Cr]**[d]	3.39[d] (m), 3.56[b] (dd)	4.90[b] (dd)	5.11[b] (d)	4.39 (m)	7.55 (m)
5	**3b[Fe]**[d]	3.00(m), 3.56[b] (dd)	5.07[b] (dd)	5.42[b] (d)	4.47 (m)	7.55 (m)
6	**3c[Cr]**[e]	3.00 (m), 3.56[b] (dd), 3.40 (m)	−	5.04[f] (t)	4.38[g] (dt)	7.55 (m)

[a] CD_3COCD_3, multiplicity is given in parentheses. [b] $^3J_{H,H}$ = 5.9 Hz. [c] $^3J_{H,H} = {}^2J_{HP}$ = 5.9 Hz. [d] OMe: δ = 3.39. [e] OMe: δ = 3.44. [f] $^4J_{H,H}$ = 2 Hz. [g] $^2J_{HP}$ = 9.3 Hz; $^3J_{H,H}$ = 5.6 Hz.

even higher frequency (δ = 6.06 ppm) for the mononuclear complex **2a** (Entry 1, Table 1).

The resonance for 6-H in the mononuclear complex **2a** presents a signal at δ = 3.73 ppm, in agreement with that previously observed for the product obtained after addition of phosphate to coordinated $[(arene)Mn(CO)_3]^+$ cations.[19c] The signals for the 6-H protons of the dinuclear complexes (Entries 2−6), which can be used as a probe for the coordination of PPh_2 to the $M'(CO)_x$ entity, display a high-frequency shift, δ = 4.30−4.47 ppm. This is consistent with the coordination of a phosphorus atom to a metal center.

Reactivity Towards (η⁶-Arene)Cr(CO)₃ Complexes

The tricarbonyl(η⁶-haloarene)chromium complexes **4a**, **4b** and **4c** reacted with PPh_2Li in THF in the presence of freshly distilled HMPT; derivatives **5a**,[20] **5b** and **5c**, respectively, were obtained in 60% yields (Scheme 3).

No reaction takes place in the absence of HMPT (which increases the nucleophilicity of the anions), emphasizing the low electrophilic nature of the Cr complexes. The easy formation of **5b** shows that steric effects, due to the presence of the *ortho*-methyl group, play no part. These metallophosphane complexes could lead to many μ-phosphido-bridged heteropolymetallic complexes. For example, we were able to synthesize such a dimetallic system incorporating a group-8 metallocene derivative.[21]

Similarly, by using $[(CO)_xM'PPh_2]Li$ (x = 5, M′ = Cr and x = 4, M′ = Fe), dimetallic complexes **6a[Cr]**, **6b[Cr]**, **6b[Fe]**[18b] (Scheme 3) were isolated in 85, 80 and 60% yields, respectively. Their ^1H NMR spectroscopic data (Entries 1, 2, 4−6, Table 2) are consistent with *ipso*-nucleophilic aromatic substitution occurring at the carbon atom bearing the fluoride atom. The same regioselectivity was clearly observed when using the *para*-disubstituted complex **4c** as the starting material. This afforded the new *para*-disubstituted complexes **5c**, **6c[Cr]** and **6c[Fe]** (Scheme 3). No *cine*- or *tele*-S_NAr was observed.[1d]

It is important to note the influence of the PPh_2 or the $PPh_2M'(CO)_x$ unit on the conformation of the $Cr(CO)_3$ tripod. Indeed the 4-H protons, *para* to the phosphanyl residue, display signals at the highest frequency (between δ = 5.80 and 6.12 ppm; Entries 1, 2, 4−6, Table 2).

This is in agreement with an *anti*-eclipsed conformation of the tripod, with respect to the bulky phosphanyl group.[1g] Similarly, the eclipsed 2-H and 6-H protons present signals at a high frequency. The biggest difference in the chemical shifts observed for two adjacent protons (3-H and 4-H) is δ = 0.92 ppm for complex **5b**. This is due to the synergic effect of the electron-donating methyl group, which favors an eclipsed conformation, and the phosphanyl group, whose steric hindrance favors an *anti*-eclipsed conformation. This confirms that the main conformation of the tripod in solution is eclipsed, with respect to the methyl group.[1d]

The IR spectra of $Cr(CO)_3$ present two well-resolved stretching modes, in accordance with the C_{3v} symmetry.[22] The absorptions are assigned to a nondegenerate symmetry vibration A1, and a doubly degenerate asymmetric vibration E.[22]

In order to evaluate the effect of complexation of the phosphorus atom by the $M'(CO)_x$ metal fragment, we compared some selected IR and ^1H NMR spectroscopic data of the mononuclear and dinuclear complexes of this chromium series (Table 3).

In all cases, a shift to higher wavenumbers is observed for the carbonyl stretching vibrations of the $Cr(CO)_3$ entity for the dimetallic complexes. This is in agreement with a stronger CO force constant, and with a decrease in the retro-donation of the chromium towards the carbonyl groups. In the NMR spectra, the 6-H protons (β to the phosphorus atom) of the dinuclear complexes present signals at a much higher frequency than those of the mononuclear complexes, e.g. the $\Delta\delta$(6-H) [$\delta(6\text{-H}_{dinuclear}) - \delta(6\text{-H}_{mononuclear})$] could reach δ = 0.57 ppm for **6c[Fe]** (Entry 8, Table 3).

In order to know more about the conformation of these complexes in the solid state, an X-ray analysis was performed on crystals of complex **6b[Cr]**. Two views of the ORTEP diagram are presented in Figure 1.

First of all, the two metallic moieties lie on both sides of the arene ring. The $Cr(CO)_3$ moiety adopts an eclipsed conformation relative to the methyl group. It is worth not-

Table 2. ^1H NMR spectroscopic data of tricarbonyl[η⁶-(1-substituted arene)]chromium complexes

Entry	Complex[a]	2-H	3-H	4-H	5-H	6-H	Ph
1	**5a**	5.56[b] (dd)	5.40[c] (dd)	5.80[c] (t)	5.40[c] (dd)	5.56[b] (dd)	7.50 (m)
2	**5b**[d]	–	4.91 (m)	5.83[c] (dd)	5.50 (m)	5.36[b] (dd)	7.50 (m)
3	**5c**[e]	5.45 (m)	5.45 (m)	–	5.45 (m)	5.45 (m)	7.55 (m)
4	**6a[Cr]**	5.86[b] (dd)	5.50[c] (dd)	6.06[c] (t)	5.50[c](dd)	5.86[b] (dd)	7.75 (m)
5	**6b[Cr]**[f]	–	5.41 (m)	6.10[c] (dd)	5.45 (m)	5.63[b] (dd)	7.70 (m)
6	**6b[Fe]**[g]	–	5.37 (m)	6.12 (m)	5.37 (m)	5.45 (m)	7.70 (m)
7	**6c[Cr]**[h]	5.90[i] (dd)	5.44[j] (d)	–	5.44[j] (d)	5.90[i] (dd)	7.55 (m)
8	**6c[Fe]**[k]	6.02[j] (dd)	5.54[j] (d)	–	5.80[j] (d)	5.98[i] (dd)	7.60 (m)

[a] CD_3COCD_3, multiplicity is given in parentheses. [b] $^3J_{H,H} = {}^3J_{PH} = 5.9$ Hz. [c] $^3J_{H,H}$=5.9 Hz. [d] Me: δ = 2.26. [e] Me: δ = 2.23. [f] Me: δ =2.11. [g] Me: δ = 2.16. [h] Me: δ = 2.33. [i] $^3J_{H,H} = {}^3J_{PH} = 6.4$ Hz. [j] $^3J_{H,H} = 6.4$ Hz. [k] Me: δ = 2.35.

Table 3. Selected IR and ^{1}H NMR spectroscopic data for (arene)chromium complexes

Entry[a][b]	Complex	ν(Cr−CO), A1 mode	ν(Cr−CO), E mode	$\Delta\nu_{A1}$, $\Delta\nu_{E}$	δ(6-H)	Δδ(6-H)
1	**5a**	1969	1899		5.56	
2	**6a[Cr]**	1978	1909	+9[c], +6[c]	5.86	+0.30
3	**5b**	1971	1895			
4	**6b[Cr]**	1972	1898	+1[d], +3[d]		
5	**6b[Fe]**	1972	1897	+1[e], +2[c]		
6	**5c**	1970	1900		5.45	
7	**6c[Cr]**	1973	1901	+3[f], +1[f]	5.90	+0.45
8	**6c[Fe]**	1976	1901	+6[g], +1[g]	6.02	+0.57

[a] IR spectra in THF [cm^{-1}]. [b] NMR spectra in $CDCl_3$ [ppm]. [c] Δν = ν**6a[Cr]** − ν**5a**. [d] Δν = ν**6b[Cr]** − ν**5b**. [e] Δν = ν**6b[Fe]** − ν**5b**. [f] Δν = ν**6c[Cr]** − ν**5c**. [g] Δν = ν**6c[Fe]** − ν**5c**.

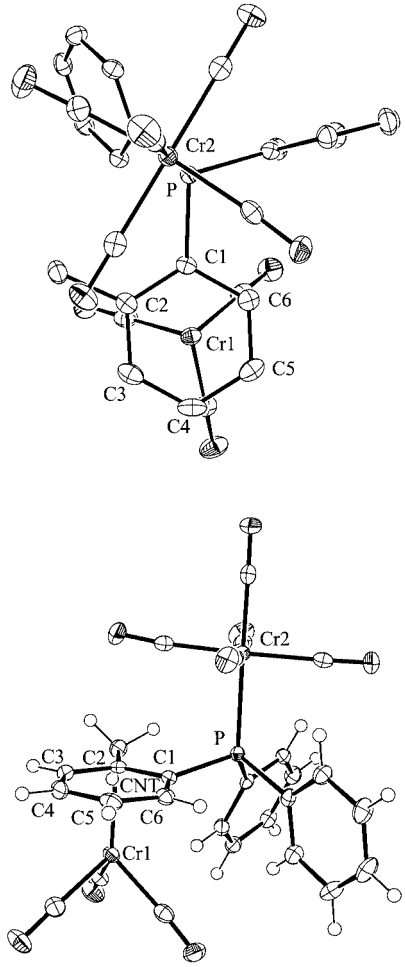
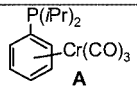
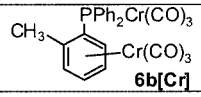


Figure 1. Two views of the ORTEP diagram of **6b[Cr]**; thermal ellipsoids are drawn at the 50% probability level; selected parameters: CNT−Cr1 1.724(2), C1−P 1.843(2), Cr2−P 2.4107(5), C1−P−Cr2 108.19(6)

ing that the longest chromium−carbon bond length is seen for Cr−C1 [2.268(2) Å], for the carbon atom substituted by the phosphane group, whereas the chromium−carbon bond length Cr−C2, for the carbon atom substituted by the methyl group, is 2.255(2) Å. The four other bond lengths are in the range 2.204−2.222 Å. Furthermore, the phosphorus atom, whose C1−P bond length is 1.843(2) Å, displays a shift of 0.471(2) Å out of the mean-aromatic plane, away from the Cr center.[23] The metal-to-ring distance is 1.724(2) Å. It is interesting to compare this structure with the tricarbonyl[(diisopropylphosphanyl)benzene]chromium structure (complex **A**), which presents a partially eclipsed conformation of the $Cr(CO)_3$ entity (midway between eclipsed and staggered, relative to the η^6-phenyl ring).[20a] In Table 4, selected bond lengths of complexes **A** and **6b[Cr]** are reported for comparison; coordination of the phosphorus substituent to $Cr(CO)_5$ does not seem to significantly affect these values. However, a small increase in the Cr−C1 bond length is induced.

Table 4. Selected bond lengths [Å] of complexes **A**[20a] and **6b[Cr]**

Complexes	 **A**	 **6b[Cr]**
Cr–C1	2.231(2)	2.2682(17)
Cr–C2	2.197(3)	2.2550(17)
Cr–C3	2.211(3)	2.2120(19)
Cr–C4	2.218(3)	2.2116(19)
Cr–C5	2.206(3)	2.2219(18)
Cr–C6	2.209 (2)	2.2039(18)
C1–P	1.840(3)	1.8431(18)
Cr–Ar	1.71	1.724(2)

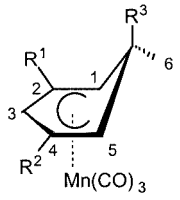
Conclusion

Metallophosphide anions readily react with electrophilic (η^6-arene)tricarbonylmanganese (by nucleophilic additions) and chromium complexes (by *ipso*-nucleophilic substitutions), and allow the easy formation of neutral dinuclear complexes, one of which has been fully characterized by X-ray analysis. Both types of reactions are useful in the synthesis of highly functionalized arylphosphane complexes, and they might therefore complement the methods previously described where nucleophilic arene derivatives are treated with electrophilic phosphanes XPR_2.

Experimental Section

General Comments: All reactions were carried out under purified argon. The solvents and eluents were dried by an appropriate procedure and distilled under argon from sodium and benzophenone immediately before use. Standard Schlenk techniques and conventional glass vessels were employed. Column chromatography was performed under argon with silica gel (70−230 mesh). Elemental analyses were carried out with an EA 1108 CHNS-O FISONS Instruments. ^{1}H (200 MHz), ^{31}P (81 MHz) and ^{13}C (50 MHz) spectra were collected with a Bruker AC 200 spectrometer. Chemical shifts are relative to internal TMS (^{1}H, ^{13}C) or external H_3PO_4 (^{31}P). IR spectra were recorded with a Nicolet 205 IR-FT. The lithium reagent $[(CO)_xM'PPh_2]Li$ (x = 5, M′ = Cr; x = 4, M′ = Fe) was prepared according to a literature method,[24] using low-chloride methyllithium (Janssen). The manganese complexes were prepared according to two different procedures, using $[BrMn(CO)_5]$ with $AlCl_3$ or $AgBF_4$ and the free arenes.[14] The syntheses of the chromium complexes were achieved by heating $[Cr(CO)_6]$ and the free arene in a 9:1 mixture of di-*n*-butyl ether and THF.[15]

(Arene)manganese Complexes. General Procedure: 5 mL of a THF solution of PPh_2Li or $[(CO)_xM'PPh_2]Li$ (1 mmol) was added dropwise to a suspension of $[(\eta^6\text{-}C_6H_4\text{-}2\text{-}R^1\text{-}4\text{-}R^2)Mn(CO)_3](PF_6)$ (1 mmol) in THF (15 mL) at −80 °C. The stirred mixture was gradually warmed to room temperature for about 5 h, and THF was then removed in vacuo. With $R^3 = PPh_2$, the crude product was dissolved in Et_2O and filtered through Celite. For the dimetallic systems [$R^3 = (CO)_xM'PPh_2$], the residue was washed with pentane and chromatographed (eluent: toluene) to give an orange-yellow powder. All complexes $[(\eta^5\text{-}C_6H_3\text{-}2\text{-}R^1\text{-}4\text{-}R^2\text{-}6\text{-}R^3)Mn(CO)_3]$ were isolated after recrystallization from toluene.

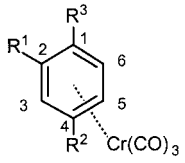


$[(\eta^5\text{-}C_6H_6\text{-}6\text{-}R^3)Mn(CO)_3]$ ($R^3 = PPh_2$: 2a): Yellow crystals (60 mg, 40% yield). IR (νCO, THF): $\tilde{\nu}$ = 2014 (w), 1935 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3): see Table 1. ^{31}P{^{1}H} NMR (CD_3COCD_3): δ = 9.9 (s) ppm. $C_{21}H_{16}MnO_3P$ (402.3): calcd. C 62.70, H 4.01; found C 62.44, H 4.14. **{$R^3 = PPh_2Cr(CO)_5$: 3a[Cr]}:** Yellow crystals (326 mg, 55% yield). IR (νCO, THF): $\tilde{\nu}$ = 2061 (m), 2020 (s), 1982 (w), 1940 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3): see Table 1. ^{31}P{^{1}H} NMR (CD_3COCD_3): δ = 62.8 (s) ppm. $C_{26}H_{16}CrMnO_8P$ (594.3): calcd. C 52.55, H 2.71; found C 52.97, H 2.77. **{$R^3 = PPh_2Fe(CO)_4$: 3a[Fe]}:** Yellow crystals (199 mg, 35% yield). IR (νCO, THF): $\tilde{\nu}$ = 2053 (m), 1978 (w), 1943 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3): see Table 1. ^{31}P{^{1}H} NMR (CD_3COCD_3): δ = 77.4 (s) ppm. $C_{25}H_{16}FeMnO_7P$ (570.2): calcd. C 52.67, H 2.83; found C 52.95, H 2.58.

$[(\eta^5\text{-}C_6H_5\text{-}2\text{-}OMe\text{-}6\text{-}R^3)Mn(CO)_3]$ {$R^3 = PPh_2Cr(CO)_5$: 3b[Cr]}: Yellow crystals (343 mg, 55% yield). IR (νCO, THF): $\tilde{\nu}$ = 2061 (m), 2019 (s), 1980 (w), 1940 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ = 3.39 (m, 4 H, OMe and 1-H) ppm, see Table 1. ^{31}P{^{1}H} NMR (CD_3COCD_3): δ = 63.4 (s) ppm. $C_{27}H_{18}CrMnO_9P$ (624.3): calcd. C 51.92, H 2.88; found C 52.20, H 2.98. **{$R^3 = PPh_2Fe(CO)_4$: 3b[Fe]}:** Not recrystallized (329 mg, 55% yield). IR (νCO, THF): $\tilde{\nu}$ = 2053 (m), 2018 (f), 1978 (m), 1940 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ = 3.39 (s, 3 H, OMe) ppm; see Table 1. ^{31}P{^{1}H} NMR (CD_3COCD_3): δ = 77.3 (s) ppm.

$[(\eta^5\text{-}C_6H_4\text{-}1\text{-}OMe\text{-}3\text{-}OMe\text{-}5\text{-}R^3)Mn(CO)_3]$ {$R^3 = PPh_2Cr(CO)_5$: 3c[Cr]}: Yellow crystalline powder (425 mg, 65% yield). IR (νCO, THF): $\tilde{\nu}$ = 2061 (m), 2018 (s), 1983 (w), 1937 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ = 3.44 (s + m, 8 H, OMe, 1-H + 5-H) ppm; see Table 1. ^{31}P{^{1}H} NMR (CD_3COCD_3): δ = 61.3 (s) ppm. $C_{28}H_{20}CrMnO_{10}P$ (654.4): calcd. C 51.39, H 3.08; found C 52.17, H 3.79.

(Arene)chromium Complexes. General Procedure: 5 mL of a THF solution of PPh_2Li or $[(CO)_xM'PPh_2]Li$ (1 mmol) was added dropwise at −80 °C to a solution of $[(\eta^6\text{-}C_6H_3\text{-}1\text{-}F\text{-}2\text{-}R^1\text{-}4\text{-}R^2)Cr(CO)_3]$ (1 mmol) in THF (15 mL) in the presence of freshly distilled HMPT (1 mmol). The stirred mixture was gradually warmed to room temperature for about 5 h, and THF was then removed in vacuo. With $R^3 = PPh_2$, the crude product was dissolved in toluene and filtered through Celite. For the dimetallic systems [$R^3 = (CO)_xM'PPh_2$], the residue was washed with pentane and chromatographed (eluent: toluene) to give a yellow powder. All complexes $[(\eta^6\text{-}C_6H_3\text{-}1\text{-}R^3\text{-}2\text{-}R^1\text{-}4\text{-}R^2)Cr(CO)_3]$ were isolated as yellow crystals after recrystallization from acetone.



$[(\eta^6\text{-}C_6H_5\text{-}1\text{-}PPh_2)Cr(CO)_3]$ (5a): Yellow crystals (238 mg, 60% yield). IR (νCO, THF): $\tilde{\nu}$ = 1969 (s), 1899 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3): see Table 2. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −1.8 (s) ppm. $C_{21}H_{15}CrO_3P$ (398.3): calcd. C 63.32, H 3.80; found C 62.93, H 4.08.

$[(\eta^6\text{-}C_6H_4\text{-}1\text{-}PPh_2\text{-}2\text{-}Me)Cr(CO)_3]$ (5b): Not recrystallized (247 mg, 60% yield). IR (νCO, THF): $\tilde{\nu}$ = 1971 (s), 1895 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ = 2.26 ppm (s, 3 H, Me); see Table 2. ^{31}P{^{1}H} NMR (CD_3COCD_3): δ = −9.8 (s) ppm.

$[(\eta^6\text{-}C_6H_4\text{-}1\text{-}PPh_2\text{-}4\text{-}Me)Cr(CO)_3]$ (5c): Yellow crystals (247 mg, 60% yield). IR (νCO, THF): $\tilde{\nu}$ = 1970 (s), 1900 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ = 2.23 (s, 3 H, Me), ppm; see Table 2. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −2.9 (s) ppm. $C_{22}H_{17}CrO_3P$ (412.3): calcd. C 64.08, H 4.16; found C 63.73, H 3.81.

$[(\eta^6\text{-}C_6H_5\text{-}1\text{-}R^3)Cr(CO)_3]$ {$R^3 = PPh_2Cr(CO)_5$: 6a[Cr]}: Yellow crystals (501 mg, 85% yield): IR (νCO, THF): $\tilde{\nu}$ = 2065 (w), 1978 (m), 1943 (s), 1909 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3): see Table 2. ^{31}P{^{1}H} NMR (CD_3COCD_3): δ = 61.5 (s) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 232 [s, Cr(*C*O)$_3$], 221.4 [d, J = 6.4 Hz, Cr(*C*O)$_5$ *trans*], 216.7 [d, J = 12.8 Hz, Cr(*C*O)$_5$ *cis*], 136.1 (d, J = 36.7 Hz, Ph *ipso*), 133.1 (d, J=11 Hz, Ph *ortho*), 131.4 (s, Ph *para*), 129.5 (d, J = 9.2 Hz, Ph *meta*), 101.5 (d, J = 24.8 Hz, C-1), 99.4 (d, J = 10 Hz, C-2 and C-6), 96.2 (s, C-4), 87.9 (d, J = 6.4 Hz, C-3 and C-5) ppm. $C_{26}H_{15}Cr_2O_8P$ (590.4): calcd. C 52.90, H 2.56; found C 52.98, H 2.69.

$[(\eta^6\text{-}C_6H_4\text{-}1\text{-}R^3\text{-}2\text{-}Me)Cr(CO)_3]$ {$R^3 = PPh_2Cr(CO)_5$: 6b[Cr]}: Yellow crystals (483 mg, 80% yield). IR (νCO, THF): $\tilde{\nu}$ = 2067 (w), 1972 (m), 1944 (s), 1898 (s) cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ = 2.11 (s, 3 H, Me) ppm; see Table 2. ^{31}P{^{1}H} NMR (CD_3COCD_3): δ = 60.21 (s) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 232.5 [s, Cr(*C*O)$_3$], 221.5 (d, J=5.5 Hz, Cr(*C*O)$_5$ *trans*), 216.8 (d, J = 12 Hz, Cr(*C*O)$_5$

cis), 134.9 (d, J = 12 Hz, Ph *ortho*), 133.9 (d, J = 36 Hz, Ph *ipso*), 133.1 (d, J = 12 Hz, Ph *ortho*), 133.0 (d, J = 35 Hz, Ph *ipso*), 131.9 (s, Ph *para*), 131.4 (s, Ph *para*), 129.7 (s, Ph *meta*), 129.5 (s, Ph *meta*), 112.7 (d, J = 8.3 Hz, C-2), 104.7 (d, J = 20 Hz, C-1), 97.9 (d, J = 14.7 Hz, C-6), 97.1 (s, C-4), 92.4 (d, J = 4.6 Hz, C-5), 87.5 (d, J = 6.5 Hz, C-3), 22.4 (s, CH_3) ppm. $C_{27}H_{17}Cr_2O_8P$ (604.4): calcd. C 53.66, H 2.84; found C 53.57, H 3.02. **{R^3 = $PPh_2Fe(CO)_4$: 6b[Fe]}:** Not recrystallized (348 mg, 60% yield). IR (νCO, THF): $\tilde{\nu}$ = 2051 (w), 1972 (s), 1943 (s), 1897 (s) cm^{-1}. ^1H NMR (CD_3COCD_3): δ = 2.16 (s, 3 H, Me) ppm; see Table 2. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ = 74.0 (s) ppm.

[(η⁶-C_6H_4-1-R^3-4-Me)$Cr(CO)_3$] {R^3 = $PPh_2Cr(CO)_5$: 6c[Cr]}: Yellow crystals (362 mg, 60% yield). IR (νCO, THF): $\tilde{\nu}$ = 2066 (w), 1973 (m), 1943 (s), 1901 (s) cm^{-1}. ^1H NMR (CD_3COCD_3): δ = 2.33 (s, 3 H, Me) ppm; see Table 2. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ = 60.5 (s) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 231.4 [s, $Cr(CO)_3$], 221.4 (d, J = 6.5 Hz, $Cr(CO)_5$ *trans*), 216.7 (d, J = 12 Hz, $Cr(CO)_5$ *cis*), 136.5 (d, J = 37 Hz, Ph *ipso*), 133.0 (d, J = 10.5 Hz, Ph *ortho*), 131.3 (s, Ph *para*), 129.4 (d, J = 9 Hz, Ph *meta*), 111.9 (s, C-4), 99.9 (d, J = 14.7 Hz, C-2 and C-6), 99.4 (d, J = 27 Hz, C-1), 89.3 (d, J = 6.5 Hz, C-3 and C-5), 21.3 (s, CH_3). $C_{27}H_{17}Cr_2O_8P$ (604.4): calcd. C 53.66, H 2.84; found C 53.80, H 2.99. **{R^3 = $PPh_2Fe(CO)_4$: 6c[Fe]}:** Yellow crystals (330 mg, 57% yield). IR (νCO, THF): $\tilde{\nu}$ = 2051 (w), 1976 (s), 1942 (s), 1901 (s) cm^{-1}. ^1H NMR (CD_3COCD_3): δ = 2.35 (s, 3 H, Me) ppm; see Table 2. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ = 78.1 (s) ppm. $C_{26}H_{17}CrFeO_7P$ (580.2): calcd. C 53.82, H 2.95; found C 54.30, H 2.99.

Crystal Structure of 6b[Cr]: Single crystals of **6b[Cr]** were obtained by recrystallization from acetone. Intensity data were collected with a Nonius Kappa CCD at 110 K. The structure was solved with a Patterson search program and refined with full-matrix least-squares methods based on F^2(SHELXL-97)[25] with the aid of the WINGX program.[26] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in their calculated positions or found in the final difference Fourier maps and refined with a riding model. CCDC-187419 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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