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The application of microwave dielectric heating to the synthesis of arene–metal complexes. Synthesis of [(η-arene)(CO) $_3$Mn]PF$_6$ complexes and [(η-arene)(η-cyclopentadienyl) Fe][PF$_6$] complexes with triphenylphosphine, *tert*-butylbenzenes and a sterically hindered phenol as arene ligands

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Abstract

Microwave-mediated syntheses of [(η-arene)(CO)$_3$Mn](PF$_6$) complexes are reported. Reaction times are reduced from several hours by conventional methods to a few minutes using an unmodified domestic microwave oven. The synthesis of a bis complexed triphenylphosphine iron sandwich complex, [{(η-C$_6$H$_5$)(η-Cp)Fe}$_2$ PC$_6$H$_5$][PF$_6$]$_2$ is reported from AlCl$_3$-catalysed ligand exchange reactions between ferrocene and M(CO)$_4$(PPh$_3$)$_2$ complexes (M = Cr, Mo, W). Sterically hindered [(η-arene)(η-Cp)Fe][PF$_6$] complexes with *tert*-butyl substituents have been prepared in moderate to excellent yields using the above microwave technique. Attempts to synthesise the methyl cyclopentadienyl analogues resulted in appreciable de-alkylation. No evidence for restricted rotation was found in the latter complexes. The direct synthesis of the 1,3,5-trimethylphenol iron sandwich complex is reported. This is the first example of a phenol complex prepared via ligand exchange reactions in iron sandwich chemistry. © 1997 Elsevier Science S.A.

1. Introduction

We have recently reported [1,2] a rapid and efficient method for the synthesis of (η-arene)(η-cyclopentadienyl) iron(II) hexafluorophosphates using microwave-mediated reactions in a simple solid CO$_2$-cooled apparatus in an unmodified domestic microwave oven. This simple technique reduces the reaction times from several hours, using conventional methods, to a few minutes, often with significant increases in yield. The work described here extends this methodology to [(η-arene)(CO)$_3$Mn][PF$_6$] complexes. These complexes have good thermal stability and are not particularly air sensitive. They are beginning to be used in the synthesis of natural products as in the total synthesis of Juvabione [3] and deoxyristomycinic acid [4] and have wide application in other areas of chemistry [5].

In addition, we report on the synthesis of some triphenyl phosphine iron sandwich complexes as well as some new (η-arene)(η-cyclopentadienyl) iron(II) salts containing sterically hindered arene ligands.

2. Results and discussion

2.1. [(η-arene)(CO)$_3$Mn][PF$_6$] complexes

The most convenient method of synthesis of [(η-arene)(CO)$_3$Mn][PF$_6$] complexes involves the aluminum chloride-catalysed ligand exchange using bromopentacarbonyl manganese [6]

$$\text{arene} + \text{BrMn(CO)}_5 \xrightarrow[(ii)\ NH_4PF_6]{(i)\ AlCl_3} [(\eta - \text{arene})(\text{CO})_3\text{Mn}] \times [\text{PF}_6] \qquad (1)$$

These reactions are normally conducted using the arene as solvent for liquid arenes, otherwise decalin is the preferred solvent The reactions involve heating for at least four hours at 100°C [7,8]. We have found that using our simple microwave technique [1,2], reaction

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times can be reduced to 3 min with yields in some instances approaching those of the more conventional method. It must be stressed that our yields were not optimised and undoubtedly modification of reaction conditions would result in improvement. Our reaction mixtures differ from the conventional method in that aluminium powder is used to increase microwave absorption. In this way, $[(\eta\text{-}C_6H_5Cl)(CO)_3Mn][PF_6]$ was prepared in 49% yield after microwave irradiation for 3 min using a medium setting for the domestic microwave oven. This compares with a 64% yield via conventional methods. Table 1 lists the yields and product characterisations. In most cases 1,2,4-trichlorobenzene was used as a solvent since this was found to be beneficial in the synthesis of $[(\eta\text{-arene})(\eta\text{-cyclopentadienyl})Fe]^+$ complexes. The exception was the synthesis of the important chlorobenzene complex where better yields were obtained without solvent. Attempts to prepare the fluorobenzene complex resulted in the formation of the phenol complex due to the extreme sensitivity of the former to hydrolysis [10]. In contrast to the $[(\eta\text{-arene})(\eta\text{-Cp})Fe]^+$ complexes (vide infra), sterically hindered arenes gave very low yields with partial dealkylation. Thus attempts to prepare the 1,3,5 tris-*tert*-butylbenzene complex resulted in a 7% yield of the *tert*-butylbenzene complex. No complexation was observed for triphenylphosphine which again contrasts with the corresponding iron sandwich complexes [2].

Attempts to prepare arene complexes of the type $[(\eta\text{-arene})(CO)_3M]$ (M = Cr, Mo, W) using the microwave technique failed due to the long recognised problem of sublimation of starting materials (for an improved method see [11]). One way of avoiding this problem is to convert $M(CO)_6$ into $M(CO)_3L_3$ where $L = NH_3$ [12], CH_3CN [13], and pyridine [14].

However, the reaction between $Cr(CO)_3(NH_3)_3$ and mesitylene using both flaked graphite and $AlCl_3$ as microwave absorbers gave none of the desired $[(\eta\text{-arene})(CO)_3Cr]$ complex.

Similar reaction using $M(CO)_4(PPh_3)_2$ complexes [15] also failed to give any product. The latter species, however, underwent an interesting reaction under conditions used to generate $[(\eta\text{-arene})(\eta\text{-Cp})Fe]^+$ complexes.

2.2. *Triphenylphosphine and related $[(\eta\text{-arene})(\eta\text{-Cp})Fe][PF_6]$ complexes*

We recently reported [2] on the $AlCl_3$-mediated ligand exchange reaction of ferrocene with triphenylphosphine. This resulted in the formation of both mono and bis complexes, the relative amounts depending on the ratio of Ph_3P to ferrocene (1:1 ratio gave 76% mono, 24% bis; 1:5 ratio gave 48% mono, 52% bis). Such mixtures are, however, difficult to separate. We have found that the ligand exchange between ferrocene (excess) and $W(CO)_4(PPh_3)_2$ gave a 50% yield of pure bis complex $[\{(\eta\text{-}C_6H_5)(\eta\text{-Cp})Fe\}_2P(C_6H_5)][PF_6]_2$. The $^{31}P\{^1H\}$ shift in solvent $[^2H_6]$-acetone of −2.8 ppm is very close to that of PPh_3 itself (−3.5 ppm, as measured in the same solvent in these laboratories), which is rather surprising.

Similar ligand exchanges using $Mo(CO)_4(PPh_3)_2$ gave mainly this bis complex but the products contained small amounts of unidentified impurities evident in the ^{31}P-NMR spectra. The above reaction therefore affords a good method for the synthesis of these interesting

Table 1
Yields [a] and physical data for $[(\eta\text{-arene})(CO)_3Mn][PF_6]$ complexes

Arene	Yield (%)	$\nu(CO)$ [b]	Mass spectral data [c]
Benzene	36 (98) [d]	2081.3, 2001.7	217.4 217)
Mesitylene	45 (98) [d]	2066.3, 1998.5	259.3 (259)
Hexamethylbenzene	56 (82) [d]	2054.3, 1995.7	301.2 (301)
Fluorene	45 (86) [e]	2068.5, 2009.5	305.3 (305)
Chlorobenzene [f]	49 (64) [g]	2086.5, 2019.2	253.2 (253)
Chlorobenzene	10	–	–
1,2-Dichlorobenzene	0.6	2090.0, 2000.0	289.4 (289)
Phenol [h]	16	2072.5, 2014.3	233.3 (233)
1,3,5-Tris-*tert*-butylbenzene	7 [i]	–	–
Triphenylphosphine	0	–	–

[a] Yields from conventional method in parentheses.
[b] Nujol mull, cm^{-1}.
[c] Mass of parent ion (M^+) by FAB technique, calculated values in parentheses.
[d] Ref. [8].
[e] Ref. [9].
[f] No solvent used.
[g] Ref. [7].
[h] Attempted synthesis of fluorobenzene complex.
[i] Elemental analysis indicates that two *tert*-butyl groups have been lost. Found: C, 38.21; H, 3.37. Calcd. for $C_{11}H_{14}F_6MnO_3P$: C, 37.34; H, 3.46.

complexes. Mechanistically it is not clear if the $AlCl_3$ removes the PPh_3 from the starting material prior to complexation or complexation by the Fe^+Cp moiety occurs before metal–phosphorus bond fission though the formation of only the bis complex suggests the latter. In the context of these phosphorus complexes we have shown that triphenylphosphine oxide also undergoes ligand exchange, but yields only the mono complex $[(\eta\text{-}C_6H_5)(\eta\text{-}Cp)FeP(O)(C_6H_5)_2][PF_6]$. Curiously the $^{31}P\{^1H\}$ shift of 29.8 ppm is again very close to that of the uncomplexed ligand (29.3 ppm).

2.3. *Sterically hindered $[(\eta\text{-arene})(\eta\text{-Cp})Fe]^+$ complexes*

Our lack of success in the synthesis of sterically crowded $[(\eta\text{-arene})(CO)_3Mn]^+$ complexes led us to examine the iron sandwich analogues. These proved surprisingly easy to make in modest to excellent yields (Table 2). Where comparisons are possible, the microwave-mediated synthesis gives considerably better yields than those using conventional methods and involves very much shorter reaction times. In the case of the 1,3,5-tri-*tert*-butyl complex, a variable temperature NMR experiment was conducted to see if such bulky substituents on the arene ring hinder rotation of the cyclopentadienyl ring. The ^{13}C signal for the Cp broadened significantly at −80°C which indicated a slowing down of the rotation, but lower temperature experiments were not possible due to solubility problems. To raise the rotational barrier, we attempted to prepare the 1,3,5-tri-*tert*-butyl complex with $C_5H_4CH_3$ as the other ligand via ligand exchange with 1,1′-dimethylferrocene. This resulted in the formation of the desired complex in 9% yield, but in addition an 11% yield of the 1,3-di-*tert*-butyl complex was obtained. Such dealkylation was not observed in the synthesis of the Cp analogue. It seems, therefore, that the loss of the *tert*-butyl group is due to release of steric strain. The two products were not separable by column chromatography, but the ^{13}C-NMR spectrum of each was sufficiently different to enable identification (Table 2). For $[(\eta\text{-}1,3,5\text{-tri-}tert\text{-butylbenzene})(\eta\text{-methylcyclopentadienyl})Fe][PF_6]$, the CH signal for the arene ligand appeared as a sharp singlet at 79.56 ppm. This indicates that there is still free rotation of the MeCp ligand at room temperature.

Hitherto, there have been no reports of direct synthesis of phenol complexes using ligand exchange reactions. Nesmeyanov [17] reported only decomposition products in his attempts to make the $[(\eta\text{-phenol})(\eta\text{-Cp})Fe][PF_6]$ complex. This complex can be made by an S_NAr displacement of chlorine from the chlorobenzene complex using NaOH in 50% aqueous acetone [18]. The reason for the failure of ligand exchange is probably the result of complexation of the oxygen site by $AlCl_3$ causing strong deactivation towards attack by the $FeCp^+$ moiety. If $AlCl_3$ complexation can be inhibited then ligand exchange should occur. Accordingly, we examined the hindered phenol, 2,4,6-trimethylphenol as a ligand and found that the corresponding $[(\eta\text{-}2,4,6\text{-trimethylphenol})(\eta\text{-Cp})Fe][PF_6]$ complex was formed in 50% yield. This is the first example of direct ligand exchange using a phenol. NMR data is presented in Table 2. Interestingly, the infrared spectrum showed a $\nu(OH)$ vibration at 3470 cm^{-1} (cf. of the phenol complex prepared in an S_NAr displacement reaction at 3495 cm^{-1}), which suggests very weak intermolecular hydrogen bonding. Thus suitably protected phenols can undergo ligand exchange, which should prove useful in future studies.

3. Experimental

Bromopentacarbonyl manganese and chromium, molybdenum and tungsten hexacarbonyls were obtained from Aldrich Chemical and used without further purification. ^{13}C- and $^{31}P\{^1H\}$-NMR spectra were run using a JEOL EX270 spectrometer. ^{31}P shifts are in ppm from H_3PO_4 and all coupling constants are in Hz. Mass spectra were obtained from a Kratos MS50 double focusing mass spectrometer with a FAB source and employing a matrix of 3-nitrobenzyl alcohol. The masses, M^+, of the ions reported were accurate to within ±0.5 mass numbers. Microanalyses were performed using in-house facilities (Perkin–Elmer, Series 2 CHN/O Analyser, Model 2400) Microwave-mediated syntheses were conducted with a conventional unmodified domestic microwave oven (Sharp Easy Chef, Model R5A53, 850 W) using the apparatus described in Ref. [1].

3.1. *Synthesis of $[(\eta\text{-arene})(CO)_3Mn][PF_6]$ complexes*

The following method for the complex was adopted generally except for the chlorobenzene complex where the solvent, 1,2,4-trichlorobenzene (TCB) was omitted. Bromopentacarbonyl manganese (0.50 g, 1.82 mmol), mesitylene (0.5 g, 4.16 mmol) and Al powder (0.5 g, 18.5 mmol) were mixed with TCB (5 g) in a small reaction beaker. Finely ground $AlCl_3$ (0.5 g, 3.76 mmol) was added and the whole thoroughly mixed. The 'cold finger' beaker [1] filled with solid CO_2 was set in place and the whole microwaved for 3 min on a medium setting. A small beaker of water was placed in the oven prior to use to absorb excess microwave radiation. On cooling, the mixture was carefully treated with ice water (30 ml) and filtered to give a yellow aqueous phase. The aqueous phase was extracted with toluene, separated, and 60% HPF_6 (0.5 g, 2.00 mmol) added. The flocculent yellow precipitate was filtered off, washed

Table 2
Yields [a] and analytical data for the synthesis [b] of [(η-arene)(η-Cp)Fe][PF$_6$] complexes with bulky substituents

Arene	Yield (%)	Analysis [c]	^{13}C-NMR data [d]							
			C1	C2	C3	C4	C5	Cp	tBu	Others
tert-Butylbenzene	77 (20) [e]	C, 45.11; H, 4.62 (C, 45.03; H, 4.78)	118.81	85.36	88.08	87.75	88.08	77.08	35.20q 30.68	–
4-*tert*-Butyltoluene	95	C, 46.21; H, 4.98 (C, 46.37; H, 5.11)	102.13	87.86	82.38	115.82	8338	76.16	33.62q 29.63	18.92 Me
1,4-di-*tert*-Butylbenzene	22	C, 49.38; H, 5.56 (C, 50.00; H, 5.96)	116.50	82.96	82.96	116.50	82.96	75.57	33.96q 31.22	–
1,3,5-tri-*tert*-Butylbenzene	35	C, 53.70; H, 6.31 (C, 53.90; H; 6.89)	116.81	79.70	116.81	79.70	116.81	76.38	35.63q 30.85	–
1,3,5-tri-*tert*-Butylbenzene [f]	9	–	117.14	79.56	117.14	79.56	117.14	96.07 C1′ [g] 76.77 C2′ 74.85 C3′	35.78q 31.09	14.26 Me
1,3-di-*tert*-Butylbenzene [f]	11	–	117.28	80.70	117.28	84.47	89.08	95.41 C1 [g] 77.30 C2′ 75.86 C3′	35.39q 30.90	13.51 Me
2,4,6-Trimethylphenol [h]	50	C, 42.12; H, 4.20 (C, 41.82; H, 4.26)	134.72	90.52	88.38	97.76	88.38	78.22	–	19.40 Me (C4) 16.65 Me (C2, 6)

[a] Literature yields in parentheses. [b] Ratio of arene/ferrocene/AlCl$_3$/Al = 1:3:6:10. Reaction time 3.5 min, medium setting. [c] Calculated values in parentheses. [d] δ_C in ppm from TMS, [^{2}H$_6$]-acetone as solvent; q = quaternary. [e] Ref. [16]. [f] Isolated as a mixture from reaction where 1,1′-dimethylferrocene replaced ferrocene. [g] Primes used for numbering substituted Cp ring. [h] M$^+$ = 257.0, calcd. value 257.

with distilled water and air-dried to give the product (0.33 g) in 45% yield.

3.2. Synthesis of $[[(\eta\text{-}C_6H_5)(\eta\text{-}Cp)Fe]_2P(C_6H_5)][PF_6]_2$

The general method adopted was as for the manganese complexes. Thus a mixture of $W(CO)_4(PPh_3)_2$ (1.64 g, 2.00 mmol), ferrocene (5 g, 26.9 mmol), $AlCl_3$ (7.1 g, 53.8 mmol) and Al powder (3 g, 111.1 mmol) in TCB (15 g) microwaved for 6 min on a medium setting yielded 1.7 g of crude product on adding 60% HPF_6 (0.5 g, 3.00 mmol). The product was purified by extraction with hot acetone, followed by filtration and careful addition of ether to give the bis complex (0.79 g, 50%) as a dark green solid. Analysis: Found C, 42.27; H, 3.32: Calcd. for $C_{28}H_{25}F_{12}Fe_2P_3$: C, 42.35; H, 3.17.

NMR data in $[^2H_6]$*-acetone.* $^{31}P\{^1H\}$-NMR, δ_P, -2.8 ppm, ^{13}C-NMR, δ_C, uncomplexed ring carbons denoted with primes. C1′ not observed, 136.91 ($^2J_{PC}$, 24.4) (C2′, 6′); 133.08 (C4′); 130.83 ($^3J_{PC}$, 9.1) (C3′, 5′); 99.28 ($^1J_{PC}$, 22.6) (C1); 92.10 ($^3J_{PC}$, 18.8) (C3, 5); 90.74 ($^4J_{PC}$, 11.0) (C4); 89.50 ($^2J_{PC}$, 28.1) (C2, 6); 78.80 Cp). The product using the chromium complex showed in addition to the bis complex small peaks at 74.3, 63.8, 31.4 and -3.6 ppm in the ^{31}P spectrum. The most downfield signal corresponds to $Cr(CO)_4(PPh_3)_2$ (73.1 ppm) [19]. In the case of the molybdenum complex, a small impurity appeared at 29.6 ppm which was not due to $Mo(CO)_4(PPh_3)_2$ (51.8) [20] and was possibly Ph_3PO.

3.3. Synthesis of $[[(\eta\text{-}C_6H_5)(\eta\text{-}Cp)Fe]P(O)(C_6H_5)_2][PF_6]$

A mixture of Ph_3PO (2.8 g, 0.01 mol), ferrocene (5.6 g, 0.03 mol), $AlCl_3$ (8.6 g, 0.06 mol) and Al powder (3.0 g, 0.111 mol) in TCB (10 g) was microwaved for 4 min on a medium oven setting. After the usual work-up and recrystallisation from acetone/ether, 0.65 g (12%) of the mono-complexed product was obtained. Mass spectral data (M^+): Found, 398.7; Calcd. 399.

NMR data in $[^2H_6]$*-acetone:* $^2H_6$-DMSO (1:1). $^{31}P\{^1H\}$-NMR, δ_P, $+29.8$ ppm. ^{13}C-NMR, δ_C, C1 not observed; 134.06 (C4′); 132.33 ($^2J_{PC}$, 10.8) (C2′, 6′); 130.06 ($^1J_{PC}$, 107.6 (C1′); 129.94 ($^3J_{PC}$, 12.7) (C3′, 5′); 90.18 (C4); 90.18 ($^3J_{PC}$, 9.8) (C3, 5); 88.98 ($^2J_{PC}$, 7.8) (C2, 6); 78.68 (Cp). Analysis: Found C, 50.31; H, 3.51; Calcd. for $C_{23}H_{20}F_6FeOP_2$: C, 50.76; H, 3.70.

3.4. Synthesis of sterically hindered $[(\eta\text{-}arene)(\eta\text{-}Cp)Fe][PF_6]$ complexes

These complexes were made using the general method described above (see Table 2 for reaction conditions).

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