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# Synthesis and reactions of polymer-supported dicarbonyl(dienyl)(triphenylphosphine)iron(0) complexes†

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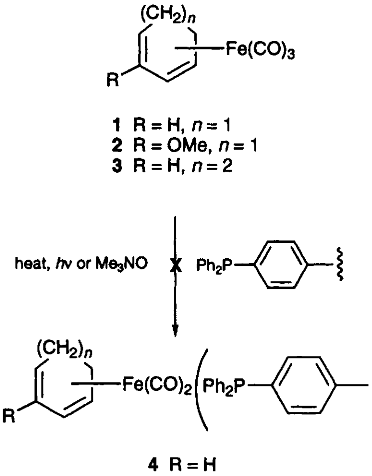
A preparative method for novel polymer-supported Fe($\eta^5$-dienyl)(CO)$_2$(PPh$_2$–polystyrene) species from [Fe($\eta^5$-dienyl)(CO)$_3$]$^+$ (dienyl = C$_6$H$_7$, 2-MeOC$_6$H$_6$ or C$_7$H$_9$) cations has been developed. The polymer-supported complexes have been characterised by iron analysis and infrared and $^{31}$P NMR spectroscopic studies and shown to undergo nucleophilic attack on the dienyl ring in a similar fashion to that of their monomeric analogues. Treatment of the resultant adducts with trifluoroacetic acid regenerated the starting dienyliron polymers.

During recent decades polymer-supported organometallic complexes have attracted considerable interest for their applications in catalysis, synthesis and as advanced materials.[1–4] For example, in many stoichiometric asymmetric syntheses two problems generally arise: (*i*) chiral reagents or auxiliaries are often expensive and cannot be recovered intact, and (*ii*) the chiral reagent, its by-product and the final product often have similar physical properties leading to tedious separation procedures. These problems may be potentially overcome with regenerable, insoluble chiral polymeric reagents.

Monomeric [Fe($\eta^5$-dienyl)(CO)$_3$]$^+$ cations are widely used reagents in organic synthesis,[5,6] employing the reactivity of the co-ordinated dienyl ring towards attack by nucleophiles. Chiral examples of such cations have been shown[7–9] to exhibit discrimination in their reactions with racemic chiral nucleophiles such as amines, amino acid esters and tertiary phosphines, and preliminary results[10] suggest that they have potential as chiral auxiliaries in the asymmetric synthesis of amines. In this paper we report the successful attachment of such ($\eta^5$-dienyl)iron cations to a polystyrene surface and demonstrate that these polymers are susceptible to attack at the dienyl ring by nucleophiles, including amines and phosphines. This opens up the possibility of the future employment of such polymers as new chiral stationary phases for the chromatographic separation of nucleophilic enantiomers or as insoluble templates for asymmetric synthesis.

## Results and Discussion

Initial studies focused on the synthesis of the neutral polymer-supported dicarbonyl($\eta^4$-diene)iron complexes **4** and **5**, from which it was hoped to generate the corresponding cationic ($\eta^5$-dienyl)iron complexes *via* hydride abstraction. However, attempts to achieve this *via* (*i*) thermal,[11,12] (*ii*) photochemical or (*iii*) Me$_3$NO-catalysed substitution[13] of a CO ligand in **1** and **2** by polystyrene-supported triphenylphosphine [equation (1)] were not successful. The infrared ν(CO) bands observed for the recovered polymers were at significantly lower frequency (*ca.* 15–35 cm$^{-1}$) than those reported for the monomeric analogue [Fe($\eta^4$-C$_6$H$_8$)(CO)$_2$(PPh$_3$)] [ν(CO) *ca.* 1981 and 1927 cm$^{-1}$][14] and were not consistent with the desired products **4** or **5**. Furthermore, these polymeric materials showed very low iron content (1.2–2.2%).



**1** R = H, *n* = 1
**2** R = OMe, *n* = 1
**3** R = H, *n* = 2

**4** R = H
**5** R = OMe

(1)

An alternative route to the desired polymer-supported ($\eta^5$-dienyl)iron complexes **12–14** was then investigated *via* treatment of the iodo complexes **9–11**[14,15] with AgBF$_4$ in CH$_2$Cl$_2$–acetone, followed by reaction with polystyrene-supported triphenylphosphine in acetone (Scheme 1). This method gave orange-yellow powders in 62–86% yields (Table 1). To assist in the spectroscopic characterisation of these polymeric products, the related monomeric [Fe($\eta^5$-dienyl)(CO)$_2$-(PPh$_3$)]BF$_4$ complexes **15–17** were also prepared as shown in Scheme 1 (**16** being described here for the first time). These latter complexes each exhibited two intense ν(CO) bands (Nujol) at 2048 and 1979, 2045 and 1985, and 2040 and 1989 cm$^{-1}$, respectively.

The polymer product **13c**, which was prepared from a 20% cross-linked polystyrene-supported triphenylphosphine (Strem), showed very weak infrared bands at 2051 and 1970 cm$^{-1}$ which are in reasonable agreement with the expected ν(CO) bands. However, the low iron content (1.2%) indicated only a *ca.* 10% coverage of the total phosphorus donor sites on the polymer chain by the organoiron group. This relatively poor co-ordination by the iron centre may reflect the more rigid and less mobile backbone in the 20% cross-linked polymer support compared to the 2% cross-linked polystyrene-supported ligands discussed below.

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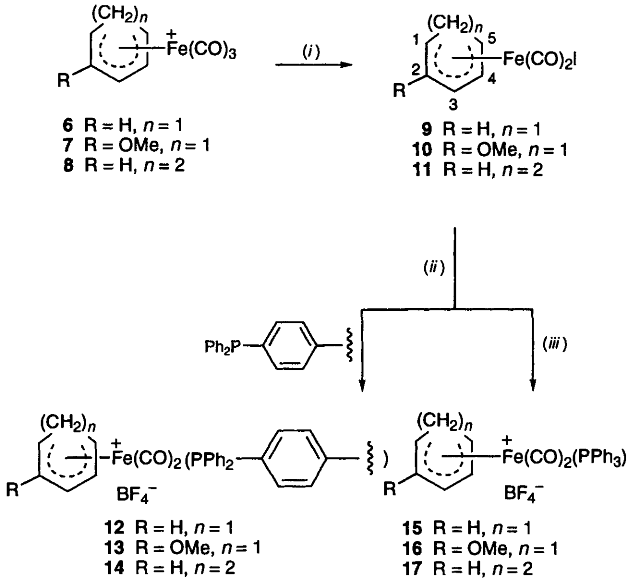
† *Non-SI unit employed:* mmHg ≈ 133 Pa.

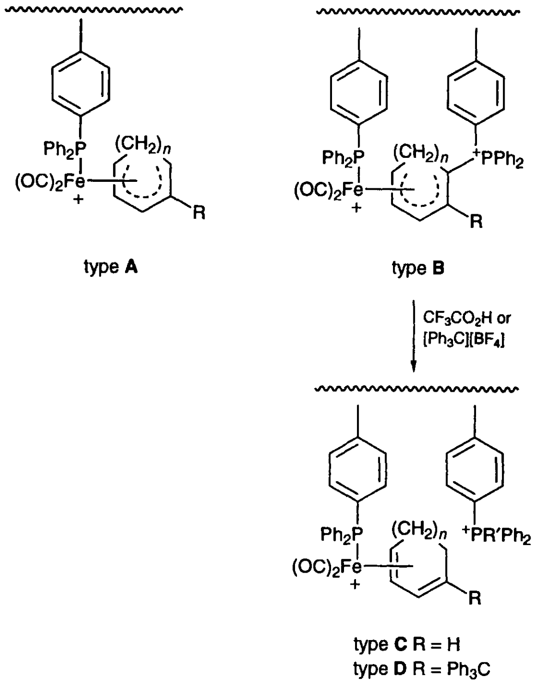
**Table 1** Yields, spectroscopic and analytical data for the polymer products **12**–**14**

| Polymer support (% cross-linkage) | Expected product | Yield (%) | $\tilde{\nu}$(CO)(Nujol)/cm$^{-1}$ | Found Fe (%)* |
|---|---|---|---|---|
| Aldrich (2) | **12a** | 79 | 2045m, 1978s (br), 1918m | 6.6 |
| Fluka (2) | **12b** | 83 | 2045m, 1977s (br), 1918w | 5.6 |
| Aldrich (2) | **13a** | 83 | 2044s, 1979s (br), 1916m | 5.2 |
| Fluka (2) | **13b** | 79 | 2048s, 1976s (br), 1915w | 5.7 |
| Strem (20) | **13c** | 62 | 2051w, 1970w | 1.2 |
| Aldrich (2) | **14a** | 86 | 2046s, 1986s (br), 1918w | 4.1 |
| Fluka (2) | **14b** | 86 | 2045s, 1982s (br), 1917w | 3.2 |

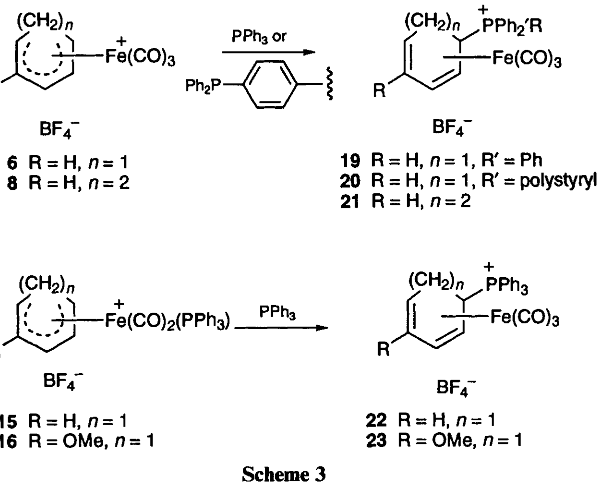
* Calc. for **12a**, **12b**, **13a**–**13c** and **14a**, **14b**: 11.7, 11.0 and 11.4%, Fe, respectively.



**Scheme 1** (*i*) KI, $Me_2CO$; (*ii*) $AgBF_4$; (*iii*) $PPh_3$



**Scheme 2**



**Scheme 3**

The polymer products similarly prepared from 2% cross-linked polystyrene-supported triphenylphosphine generally exhibited strong ν(CO) bands at *ca.* 2045 and 1980 cm$^{-1}$, consistent with the formation of the desired ($\eta^5$-dienyl)iron complexes **12**–**14** (type **A** in Scheme 2). The iron analyses for the ($\eta^5$-cyclohexadienyl)iron polymers **12a**,**12b** and **13a**,**13b** (5.2–6.6%) were consistent with 47–56% coverage of the phosphorus sites on the polymer chains. The somewhat lower coverage in the related ($\eta^5$-cycloheptadienyl)iron polymers **14a** and **14b** (28–36%) may be associated with the greater steric bulk of the cycloheptadienyl reagent **11**.

However, the presence for each of these polymeric products of additional ν(CO) bands at *ca.* 1978 and 1918 cm$^{-1}$ indicated the presence also of a ($\eta^4$-diene)iron complex species. A possible candidate for this impurity could be a phosphonium adduct of type **B**, arising from attack on the dienyl ring of the initial polymer complex (type **A**) by an adjacent unco-ordinated $PPh_3$ group on the polymer backbone (Scheme 2).

In order to provide further information concerning the structure of the polymer-supported organoiron products from these reactions, the model compounds **19**–**23** were synthesised as shown in Scheme 3 and their $^{31}$P NMR and ν(CO) spectra compared with those of the iron polymer products (Table 2). Compounds **16**, **22** and **23** have not been previously reported. *In situ* infrared and $^1$H NMR spectroscopic data for the ($\eta^4$-diene)iron phosphonium adducts **19** and **21** indicated that the reactions of the cationic tricarbonyl ($\eta^5$-dienyl)iron substrates **6** and **8** with $PPh_3$ proceeded to completion. In contrast, the reactions of the dicarbonyl($\eta^5$-dienyl)(triphenylphosphine)iron complexes **15** and **16** with $PPh_3$ were reversible processes and mixtures of the starting dienyl salts and the novel adducts **22** and **23** were obtained (Table 2). These relative equilibrium constants for phosphonium adduct formation were further supported by electrospray mass spectroscopic (ESMS) studies. While the ESMS of adducts **19** and **21** exhibited strong molecular $M^+$ ions for the intact phosphonium adducts (as well as $[M - PPh_3]^+$), **22** and **23** both showed $[M - PPh_3]^+$ as the base peak, with only a weak molecular ion peak $M^+$ for **22** and none for **23**. This is not surprising since substitution of a CO

**Table 2** Infrared and $^{13}$P NMR spectroscopic data for selected compounds

| | | $\delta_P$ | |
|---|---|---|---|
| Compound | $\tilde{\nu}$(CO)(Nujol)/cm$^{-1}$ | $Me_2CO$ | Solid state |
| Phosphorus species | | | |
| $PPh_3$ | | −4.3 | −9.5 |
| $PPh_3O$ | | 26.5 | |
| $[PPh_3(CPh_3)][BF_4]$ | | | 23.2 |
| Polystyrene-supported $PPh_3$ | | | 27.2[a], −5.8[b] |
| (Aldrich) | | | 27.2[a], −6.1[b] |
| (Fluka) | | | 30.4, −5.8[b] |
| Polystyrene-supported $PPh_3$ + $CF_3CO_2H$ | | | |
| Model complexes | | | |
| **15** | 2048, 1979 | 61.7 | 64.3, 16.1[c], 5.1[c] |
| **16** | 2045, 1985 | 59.8 | 54.3 |
| **17** | 2040, 1989 | 60.9 | 57.8, 5.0[c] |
| **19** | 2057, 1986 | 29.3 | 27.5 |
| **20** | 2052, 1965 | | 26.8, −5.6[b] |
| **21** | 2054, 1982 | | 28.1 |
| **22** | 1979, 1919 | 70.1[d], 61.7[e], 27.4[f] | |
| **23** | (MeCN) 2044w, 1998 (sh), 1982s, 1922s | | 69.0[d], 25.0[f], −9.6[g] |

[a] Minor peak, assigned as O=PPh$_2$–polystyrene, see ref. 13. [b] Assigned as free polystyrene-supported PPh$_3$. [c] Minor impurity peak. [d] Assigned as ($\eta^4$-diene–PPh$_3$)Fe(CO)$_2$(*P*Ph$_3$). [e] Minor peak, assigned as ($\eta^5$-dienyl)Fe(CO)$_2$(PPh$_3$). [f] Assigned as ($\eta^4$-diene–*P*Ph$_3$)Fe(CO)$_2$(PPh$_3$). [g] Assigned as free PPh$_3$.

ligand with an electron-donating PPh$_3$ ligand should increase the electron density on the diene rings in **22** and **23**, facilitating dissociation of the PPh$_3$ substituent from the ring.

### Model compounds

In the solid state the $^{31}$P NMR resonances for free PPh$_3$ and polystyrene-supported triphenylphosphine occur in the region δ −5.8 to −9.5 (Table 2). The spectra also showed that some of the polystyrene-supported triphenylphosphine had been oxidised to the corresponding phosphine oxide, O=PPh$_2$ (δ 27.2, *cf.* O=PPh$_3$ at δ 26.5 in the solution state).

The $^{31}$P NMR resonances for the monomeric and polymer-supported phosphines and their phosphonium adducts were very similar (chemical shift differences < 5 ppm). In general, a PPh$_3$ attached to the diene ring of a tricarbonyl($\eta^4$-diene)iron complex, as in complexes **19**–**21**, showed $^{31}$P NMR signals in the range δ 26–28 (Table 2), *i.e.* they are shifted strongly downfield (by *ca.* 37 ppm) compared to free PPh$_3$. This downfield shift was even greater than that (33 ppm) caused by tritylation of PPh$_3$ with the cation [Ph$_3$C$^+$], confirming that ($\eta^4$-diene)Fe(CO)$_3$ groups are strongly electron withdrawing, as has been suggested from other studies.[16]

The $^{31}$P NMR signals of PPh$_3$ co-ordinated to the iron in compounds **22** and **23** were shifted significantly downfield (by *ca.* 43 ppm) compared to the diene ring-bound PPh$_3$. It was therefore easy to distinguish whether a phosphorus donor was attached to the iron or to the diene ring of such complexes. On the other hand, the chemical shift of the phosphorus centre of PPh$_3$ on the diene ring was only slightly affected by replacing a CO ligand by PPh$_3$. Thus, it was shifted slightly upfield for **22** compared to **19**, as expected for the increase in the electron density within the complex arising from such a ligand substitution.

The monomeric model complexes having structures closest to the expected polymer products are **15**–**17**. Both the solution and solid-state $^{31}$P NMR spectra of these showed the expected signal at δ *ca.* 60 for [Fe($\eta^5$-dienyl)(CO)$_2$(*P*Ph$_3$)]$^+$. The $^{31}$P NMR chemical shift of the PPh$_3$ group bound to the Fe is quite sensitive to whether the Fe is attached to a diene or a dienyl ring. These differences in the chemical shifts can therefore be very useful in distinguishing the nature of complexes such as **15** from **19** and **22**.

**Table 3** Phosphorus-31 NMR spectroscopic data for the crude polymer products **12**–**14**

| Polymer product | $\delta_P$(solid state) |
|---|---|
| **12a** | *ca.* 65 (sh),[a] 59.7,[b] 26.0,[c] 10.3,[d] −5.1[e] |
| **12b** | 66.6,[a] 60.0,[b] 26.5,[c] −4.5[e] |
| **13a** | 65.0,[a] 59.7,[b] 25.6 (sh),[c] 16.9[d] |
| **13b** | 67.6,[a] 58.5,[b] 24.4,[c] 8.4,[d] −6.3[e] |
| **14a** | *ca.* 65 (sh),[a] 56.8,[b] 26.2,[c] 10.5[d] |
| **14b** | *ca.* 65 (sh),[a] 60.6,[a] 25.6,[c] 9.0,[d] −5.6[e] |

[a] Assigned as (polystyrene–Ph$_2$P–diene)Fe(CO)$_2$(*P*Ph$_2$–polystyrene). [b] Assigned as (dienyl)Fe(CO)$_2$(PPh$_2$–polystyrene). [c] Assigned as (polystyrene–Ph$_2$*P*–diene)Fe(CO)$_2$(PPh$_2$–polystyrene) or O=PPh$_2$–polystyrene. [d] Unknown peak. [e] Free polystyrene-supported PPh$_3$.

### Spectroscopic characterisation of the modified polymer products

The $^{31}$P NMR (solid-state) spectroscopic data for the crude polymer products obtained from the reactions shown in Scheme 1 are summarised in Table 3. From a comparison of the infrared ν(CO) and $^{31}$P NMR spectroscopic data for the polymer products in Tables 1 and 3 with those of related model compounds (Table 2), these new modified polymer products can be concluded to contain two different structural types, identified as **A** and **B** in Scheme 2. The ν(CO) bands at *ca.* 2045 and 1980 cm$^{-1}$ and the $^{31}$P NMR resonances at δ *ca.* 60 are consistent with a polystyrene-supported PPh$_3$ bound to the iron atom, which is co-ordinated to a ($\eta^5$-dienyl)iron ring (structural type **A**). On the other hand, ν(CO) bands also observed at *ca.* 1976 and 1918 cm$^{-1}$ and $^{31}$P NMR resonances at δ *ca.* 65 and 25 are consistent with the presence also of polystyrene-supported triphenylphosphine attached to both the iron atom (co-ordinated to a $\eta^4$-diene ring) and to the carbon-5 centre on the diene ring (structural type **B**). Consistent with this structural hypothesis was the observation that treating the crude polymer products **12**–**14** with an excess of trifluoroacetic acid in dichloromethane caused the disappearance, or a decrease in intensity, of the ν(CO) band at 1918 cm$^{-1}$ (associated with the suggested diene impurities), and an increase in intensity of the band at *ca.* 2045 cm$^{-1}$ associated with the dienyl product (Table

4). [The other expected ν(CO) band for these diene complex impurities at *ca.* 1980 cm$^{-1}$ is masked by the dienyl product band in the same region.] The $^{31}$P NMR signal at δ *ca.* 65 for (polystyrene–$Ph_2P^+$–diene)$Fe(CO)_2$(*P*$Ph_2$–polystyrene) also disappeared and a new peak at δ *ca.* 29 (for polystyrene–*P*$Ph_2H$) was observed after the trifluoroacetic acid treatment. This suggested that η$^5$-dienyl complexes of type **C** were formed (Scheme 2). Similar cleavage of phosphonium adducts of related monomeric diene iron complexes with trifluoroacetic acid to regenerate dienyl complexes has been previously described.[17]

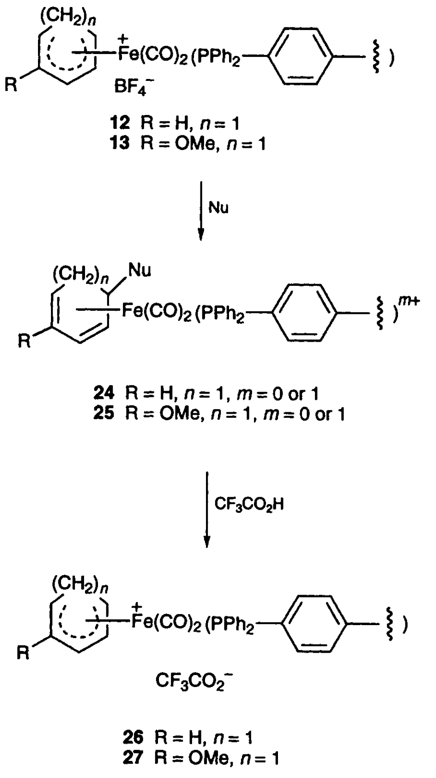
Removal of the phosphonium ion feature of structural type **B** from the crude polymer products could also be achieved by refluxing the polymers with an excess of $[Ph_3C][BF_4]$ in dichloromethane for *ca.* 1 h. The spectroscopic and analytical results for the polymer products obtained from such $[Ph_3C][BF_4]$ treatment are summarised in Table 5. Infrared spectroscopic data supported regeneration of the polymer-bound dienyliron complexes of type **D**, in which uncoordinated pendant $PPh_2$ groups are presumably blocked with a trityl moiety (Scheme 2). In addition, the $^{31}$P NMR spectra showed new resonances in the range δ 24.8–26.0 which could be attributed to polystyrene–*P*$Ph_2$–$CPh_3$.

The similar spectroscopic results obtained for the polymer products after $[Ph_3C][BF_4]$ treatment (Table 5) compared to those after trifluoroacetic acid treatment (Table 4) suggested that tritylation also resulted in polymers containing structural features of types **A** (major) and **B** (minor). After treatment with trifluoroacetic acid or $[Ph_3C][BF_4]$ the polymer products showed a slight decrease in their iron content.

### Nucleophilic addition to polymer-supported dienyl iron complexes

Monomeric tricarbonyl(η$^5$-dienyl)iron cations are known to react at the dienyl ring with a wide range of nucleophiles.[9,18–22] Related dicarbonyl(η$^5$-dienyl)(triphenylphosphine)iron complexes also react with nucleophiles, although less rapidly due to the electron-donating effect of the $PPh_3$ ligand.[14,22] Therefore, attachment of polystyrene-supported triphenylphosphine to such dienyliron complexes should provide materials which retain reactivity towards nucleophiles. Reactions of the above novel polymer-supported dienyliron complexes **12a** and **13a** with various nucleophiles such as $H^-$, $PBu_3$, $PPh_3$, benzylamine and glycine ethyl ester were therefore examined in dichloromethane or dichloromethane–water at room temperature in order to test this hypothesis (Scheme 4). These reactions were readily monitored by infrared spectroscopy and the results are summarised in Table 6.

Addition of $NaBH_4$ to the crude polymer **12a** in water–dichloromethane caused the ν(CO) bands to shift from 2045 and 1978 cm$^{-1}$ to lower frequencies at 1960 and 1905 cm$^{-1}$, as expected for the formation of the neutral (η$^4$-diene)iron adduct **24** (Nu = H, *m* = 0). These product ν(CO) bands are very similar to those reported for the analogous monomeric complex $[Fe(\eta^4\text{-}C_6H_8)(CO)_3]$.[23] Reaction of benzylamine with the polymers **12a** and **13a** in dichloromethane gave the related ring adducts **24** (Nu = $NHCH_2Ph$, *m* = 0) and **25** (Nu = $NHCH_2Ph$, *m* = 0), respectively, as indicated again by the shift to lower frequencies of the ν(CO) bands (Table 6). The product ν(CO) bands in both cases at 1970 and *ca.* 1910 cm$^{-1}$



**Scheme 4**

**Table 4** Infrared and $^{31}$P NMR spectroscopic data and iron content of the polymer products after treatment with trifluoroacetic acid

| Starting polymer | Polymer after treatment | $\tilde{\nu}$(CO)(Nujol)/cm$^{-1}$ | $\delta_P$(solid state) | Found Fe(%)[a] |
|---|---|---|---|---|
| **12a** | **12a′** | 2045s, 1978s, 1921w | 61.5,[b] 30.2 (sh),[c] 24.0,[d], 9.7,[e] −6.3[f] | 5.6 |
| **12b** | **12b′** | 2045s, 1980s, 1920w | 61.0,[b] 29.6,[c] 26.7,[d] 1.2[e] | 5.3 |
| **13a** | **13a′** | 2042, 1985 | 59.6,[b] 30.0,[c] 16.7[e] | 4.8 |
| **13b** | **13b′** | 2043s, 1985s, 1920w | 56.0,[b] 28.9 (sh),[c] 25.0,[d] 17.8[e] | 5.1 |
| **14a** | **14a′** | 2045, 1986 | 59.7,[b] 29.9,[c] 26.4,[d] 9.6,[e] −4.8[f] | 3.0 |
| **14b** | **14b′** | 2045s, 1986s, 1923w | 58.6,[b] 29.2,[c] 25.0,[d] 10.2[e] | 2.8 |

[a] Calc. for **12b′** and **13b′**: 11.7 and 11.0%, Fe, respectively. [b] Assigned as (dienyl)$Fe(CO)_2$($PPh_2$–polystyrene). [c] Assigned as polystyrene–$PPh_2H$. [d] Assigned as (polystyrene–*P*$Ph_2$–diene)$Fe(CO)_2$(*P*$Ph_2$–polystyrene) or O=$PPh_2$–polystyrene. [e] Unknown peak. [f] Free polystyrene-supported $PPh_3$.

**Table 5** Infrared and $^{31}$P NMR spectroscopic data and iron content of polymer products after tritylation

| Starting polymer | Tritylated polymer | $\tilde{\nu}$(CO)(Nujol)/cm$^{-1}$ | $\delta_P$(solid state) | Found Fe (%) |
|---|---|---|---|---|
| **12a** | **12a″** | 2046s, 1979s, 1919w | 59.5,[a] 27.1,[b] 24.8,[c] 8.2[d] | 5.3 |
| **13a** | **13a″** | 2048s, 1982s, 1918w | 57.2,[a] 25.0,[c] 15.6[d] | 4.8 |
| **14a** | **14a″** | 2046s, 1985s, 1923w | 56.0,[a] 26.0,[b,c] 8.9,[d] −6.9[e] | 4.8 |

[a] Assigned as (dienyl)$Fe(CO)_2$($PPh_2$–polystyrene). [b] Assigned as (polystyrene–*P*$Ph_2$–diene)$Fe(CO)_2$(*P*$Ph_2$–polystyrene) or O=$PPh_2$–polystyrene. [c] Assigned as $Ph_3C$–*P*$Ph_2$–polystyrene. [d] Unknown peak. [e] Polystyrene-supported $PPh_3$.

**Table 6** Infrared spectral data for the polymers **24** and **25** obtained after addition of nucleophiles to **12a** and **13a**, respectively

| Starting polymer | Nucleophile | Polymer product | $\tilde{\nu}$(CO)(Nujol)/cm$^{-1}$ |
|---|---|---|---|
| **12a** | $NaBH_4$ | **24** Nu = H, *m* = 0 | 1960, 1905 |
| | $H_2NCH_2Ph$ | **24** Nu = $NHCH_2Ph$, *m* = 0 | 1970, 1910 |
| | $PBu_3$ | **24** Nu = $PBu_3$, *m* = 1 | 1975, 1920 |
| | $PPh_3$ | **24** Nu = $PPh_3$, *m* = 1 | 1976, 1918 |
| **13a** | $H_2NCH_2Ph$ | **25** Nu = $NHCH_2Ph$, *m* = 0 | 1970, 1907 |
| | $H_2NCH_2CO_2Et$ | **25** Nu = $NHCH_2CO_2Et$, *m* = 0 | 1976, 1913;<br>1753 ($CO_2Et$) |

are similar to those reported for the analogous monomer adduct [Fe{$\eta^4$-$C_6H_7(NHCH_2Ph)$}$(CO)_3$].[17] Similarly, addition of glycine ethyl ester to the polymer **13a** yielded the neutral diene ring adduct **25** (Nu = $NHCH_2CO_2Et$, *m* = 0), as confirmed by the ν(CO) changes shown in Table 6. A strong ν(CO) band was also observed at 1753 cm$^{-1}$ for adduct **25** characteristic of the $CO_2Et$ group.

On the other hand, the polymers obtained from the analogous addition of tributyl- and triphenyl-phosphine to **12a** showed ν(CO) bands at 1975, 1920 and 1976, 1918 cm$^{-1}$, respectively. These slightly higher-wavenumber ν(CO) bands are consistent with the formation of the cationic phosphonium diene adducts **24** (Nu = $PBu_3$, *m* = 1) and **24** (Nu = $PPh_3$, *m* = 1). Subsequent treatment of adducts **24** and **25** with trifluoroacetic acid regenerated the corresponding starting ($\eta^5$-dienyl)iron polymers **26** and **27** (Scheme 4), as indicated by the reappearance of strong ν(CO) bands at *ca.* 2045 and 1976 cm$^{-1}$ and at *ca.* 2040 and 1982 cm$^{-1}$, respectively. However, the retention of a weak ν(CO) band at *ca.* 1918 cm$^{-1}$ suggested that some diene impurities also remained.

## Conclusion

A preparative method for novel polymer-supported ($\eta^5$-dienyl)Fe$(CO)_2(PPh_2$–polystyrene) species from [Fe($\eta^5$-dienyl)$(CO)_3$]$^+$ (dienyl = $C_6H_7$, 2-Me$OC_6H_6$ or $C_7H_9$) cations has been developed. In most cases these products also contained a ($\eta^4$-diene)iron phosphonium adduct. However, the diene phosphonium adducts could be converted into the desired dienyl complexes *via* treatment with trifluoroacetic acid or by tritylation. These polymer-supported dienyl complexes undergo nucleophilic attack on the dienyl ring in a similar fashion to their monomeric analogues. By subsequent treatment with trifluoroacetic acid the starting dienyliron polymers can be readily regenerated and the nucleophile released.

These results suggest that chiral examples of such polymers, *e.g.* **13** which possesses planar chirality, may have potential as stationary phases for the chromatographic separation of chiral molecules such as amines and tertiary phosphines, or as templates for asymmetric synthesis. Exploration of these potential applications is currently under way.

## Experimental

### General procedures

Melting points were determined on a Gallenkamp capillary apparatus and were uncorrected. Infrared spectra were recorded on a Bio-Rad FTS-5 or a Bomem Gram-Michelson Fourier-transform spectrometer and calibrated against a polystyrene standard. The spectra were measured in a $CaF_2$ liquid cell as solutions in MeCN or $CH_2Cl_2$, as Nujol mulls or as KBr pellets. Proton NMR spectra were recorded on Varian Unity spectrometer operating at 400 MHz. Signals are described in terms of chemical shift (δ) from $SiMe_4$. The assignments for most spectra were confirmed by their related correlation (COSY) spectra. The $^{13}$C NMR spectra were recorded on a Varian Unity spectrometer operating at 100 MHz. The assignments for most spectra were confirmed by their related distortionless enhancements by polarisation transfer (DEPT) spectra. The $^{31}$P NMR spectra were recorded at the School of Chemistry, University of New South Wales, using a Bruker MSL 300 spectrometer operating at 120 MHz. Solution spectra were measured in acetone with an external $D_2O$ lock and referenced to 85% $H_3PO_4$ (δ 0.0), solid-state spectra with cross polarisation magic-angle spinning and external referencing to $NH_4H_2PO_4$ (δ 1.0). Mass spectra were recorded on a VG Quattro Triple Quadrupole spectrometer in the electrospray (ES) mode from MeCN solution, using low skimmer voltages (20–30 V) and procedures described elsewhere.[24]

Iron analyses for the polymer-supported complexes were carried out by digestion in concentrated $HNO_3$–HCl solution and quantification by atomic absorption spectroscopy.

### Synthesis of metal complexes

The known [Fe($\eta^4$-diene)$(CO)_3$] and [Fe($\eta^5$-dienyl)$(CO)_3$]$^+$ complexes were prepared and purified as previously described.[15,23] The related iododicarbonyl [Fe($\eta^5$-dienyl)$(CO)_2$I] complexes were synthesised by a modification of the reported procedures,[14,15] and [Fe($\eta^5$-dienyl)$(CO)_2(PPh_3)$]$^+$ from the corresponding [Fe($\eta^5$-dienyl)$(CO)_2$I] by a modification of the literature method.[14] In our hands the previously described methods[14,15] were difficult to reproduce. Glycine ethyl ester was obtained by treatment of glycine ethyl ester hydrochloride (Aldrich) in $CHCl_3$ with anhydrous $NH_3$. Polymer-supported triphenylphosphines were obtained from: (*i*) Aldrich, 9.5% polystyrene, 2% cross-linkage (divinylbenzene), 0.00306 mmol $PPh_3$ per g of polymer, fine orange-yellow powder; (*ii*) Fluka; 9.5% polystyrene, 2% cross-linkage (divinylbenzene), 0.00306 mmol $PPh_3$ per g of polymer, orange-yellow powder, finely ground prior to use, and (*iii*) Strem; polystyrene–divinylbenzene copolymer with 20% cross-linked, off-white beads, 20–60 mesh, finely ground prior to use. Triphenyl(triphenylmethyl)phosphonium tetrafluoroborate was prepared from the reaction of triphenylphosphine with triphenylmethyl tetrafluoroborate in dichloromethane. Polystyrene-supported triphenylphosphonium trifluoroacetate was prepared by stirring a suspension of polystyrene-supported triphenylphosphine and trifluoroacetic acid in dichloromethane for 50 min. The polymer product was filtered off, then rinsed with dichloromethane and dried.

### Synthesis of [Fe($\eta^5$-dienyl)$(CO)_2$I] complexes

**Dicarbonyl($\eta^5$-cyclohexadienyl)iodoiron 9.** Potassium iodide (0.94 g, 5.66 mmol) was added to a pale orange-yellow solution of tricarbonyl($\eta^5$-cyclohexadienyl)iron tetrafluoroborate **6** (1.15 g, 3.76 mmol) in acetone (120 cm$^3$). The mixture, which turned dark brown immediately, was stirred at 28–30 °C for 3 h under dinitrogen. Rotary evaporation gave a dark brown, oily solid (1.99 g). Purification of this crude solid by column chromatography on silica gel (70–230 mesh) using benzene–hexane (1 : 1) as eluent and collection of the brown band gave the desired compound **9** as a dark brown, crystalline solid (0.91 g, 78%). $\tilde{\nu}$(CO)(CH$_2$Cl$_2$)/cm$^{-1}$ 2036, 1994 [lit.,[15] $\nu$(CO)(KBr)/cm$^{-1}$ 2041, 1992]; $\delta_H$[(CD$_3$)$_2$CO] 7.21 [1 H, t, $J$(H$^2$H$^3$) = $J$(H$^3$H$^4$) = 6.3, H$^3$], 5.49 [2 H, t, $J$(H$^1$H$^2$) = $J$(H$^2$H$^3$) = $J$(H$^3$H$^4$) = $J$(H$^4$H$^5$) = 6.3, H$^2$ and H$^4$], 3.29 [2 H, t, $J$(H$^1$H$^{6'}$) = $J$(H$^5$H$^{6'}$) 6.3, H$^1$ and H$^5$], 2.84 [1 H, dt, $J$(H$^1$H$^{6'}$) = $J$(H$^5$H$^{6'}$) 6.3, $J$(H$^6$H$^{6'}$) = 14.2, H$^{6'}$] and 2.13 [1 H, d, $J$(H$^6$H$^{6'}$) = 14.2 Hz, H$^6$]; *m/z* 317 ($M^+$, 34), 289 ([$M$ − CO]$^+$, 62), and 163 ([$M$ − 2CO − I]$^+$, 90%)

**Dicarbonyliodo(η$^5$-2-methoxycyclohexadienyl)iron 10.** This compound was prepared from tricarbonyl(η$^5$-2-methoxycyclohexadienyl)iron hexafluorophosphate **7** using the general procedure described above as a dark brown, crystalline solid (300 mg, 83%) (Found: C, 30.6; H, 2.7; I, 36.5. Calc. for C$_9$H$_7$FeIO$_3$: C, 31.1; H, 2.6; I, 36.5%). $\tilde{\nu}$(CO)(CH$_2$Cl$_2$)/cm$^{-1}$ 2033, 1989; (MeCN) 2031, 1985; $\delta_H$[(CD$_3$)$_2$CO] 7.04 [1 H, d, $J$(H$^3$H$^4$) = 6.3, H$^3$], 5.60 [1 H, t, $J$(H$^3$H$^4$) = $J$(H$^4$H$^5$) = 6.3, H$^4$], 3.66 (3 H, s, MeO), 3.37 [1 H, t, $J$(H$^4$H$^5$) = $J$(H$^5$H$^{6'}$) = 6.3, H$^5$], 2.99 [1 H, d, $J$(H$^1$H$^{6'}$) = 6.3, H$^1$], 2.79 [1 H, dd, $J$(H$^1$H$^{6'}$) = $J$(H$^5$H$^{6'}$) = 6.3, $J$(H$^6$H$^{6'}$) 12.6, H$^{6'}$] and 2.13 [1 H, d, $J$(H$^6$H$^{6'}$) = 12.6 Hz, H$^6$]; $\delta_C$(CDCl$_3$) 212.0 (CO), 140.0 (C), 72.9 (CH), 67.6 (CH), 55.3 (MeO), 54.2 (CH), 50.8 (CH) and 25.6 (CH$_2$); *m/z* 293 ([$M$ + H − 2CO]$^+$, 5) and 165 ([$M$ − 2CO − I]$^+$, 50%).

**Dicarbonyl(η$^5$-cycloheptadienyl)iodoiron 11.** This compound was prepared from tricarbonyl(η$^5$-cycloheptadienyl)iron tetrafluoroborate **8** using the general procedure described above as a dark brown, crystalline solid (1.02 g, 86%). $\tilde{\nu}$(CO)(CH$_2$Cl$_2$)/cm$^{-1}$ 2034, 1993; (MeCN) 2032, 1989 [lit.,[14] $\tilde{\nu}$(CO)(KBr)/cm$^{-1}$ 2041, 1992]; $\delta_H$[(CD$_3$)$_2$CO] 7.08 [1 H, t, $J$(H$^2$H$^3$) = $J$(H$^3$H$^4$) = 6.3, H$^3$], 5.73 [2 H, t, $J$(H$^1$H$^2$) = $J$(H$^2$H$^3$) = $J$(H$^3$H$^4$) = $J$(H$^4$H$^5$) = 6.3, H$^2$ and H$^4$], 3.97 (2 H, br s, H$^1$ and H$^5$), 2.42 [2 H, dt, $J$(H$^6$H$^7$) = $J$(H$^{6'}$H$^{7'}$) = 3.6, $J$(H$^6$H$^{6'}$) = $J$(H$^7$H$^{7'}$) = 9.6, H$^{6'}$ and H$^{7'}$] and 1.45 [2 H, d, $J$(H$^6$H$^{6'}$) = $J$(H$^7$H$^{7'}$) = 9.6, H$^6$ and H$^7$]; *m/z* 332 ($M^+$, 5) and 304 ([$M$ − CO]$^+$, 22%).

**Dicarbonyl(η$^5$-cyclohexadienyl)(triphenylphosphine)iron tetrafluoroborate 15.** A dark brown solution of complex **9** (1.06 g, 3.34 mmol) in dichloromethane (20 cm$^3$) was added to a solution of AgBF$_4$ (0.65 g, 3.34 mmol) in acetone (40 cm$^3$) while stirring under argon. The resulting orange-brown mixture was stirred at room temperature for 15 min, then filtered through a fritted disc (to remove the precipitate of AgI) and passed slowly, with vacuum suction, into a Schlenk flask containing a clear solution of triphenylphosphine (0.87 g, 3.34 mmol) in acetone (40 cm$^3$). After stirring at room temperature for 1 h the resulting orange-yellow solution was rotary evaporated to dryness giving a dark orange-yellow oily solid (2.68 g). Recrystallisation of this oily solid from CH$_2$Cl$_2$–Et$_2$O yielded compound **15** as a light yellow powder (1.24 g, 69%). $\tilde{\nu}$(CO)(CH$_2$Cl$_2$)/cm$^{-1}$ 2048, 2006; (MeCN); 2046, 2002; (Nujol) 2048, 1979. Its $^1$H NMR spectrum was similar to that reported.[14] $\delta_H$[(CD$_3$)$_2$CO] 7.54–7.71 (15 H, m, PPh$_3$), 7.38 [1 H, t, $J$(H$^2$H$^3$) = $J$(H$^3$H$^4$) = 6.0, H$^3$], 5.50 [2 H, t, $J$(H$^2$H$^3$) = $J$(H$^1$H$^2$) = $J$(H$^3$H$^4$) = 6.0, H$^2$ and H$^4$], 3.86 [2 H, t, $J$(H$^1$H$^2$) = $J$(H$^1$H$^{6'}$) = $J$(H$^4$H$^5$) = $J$(H$^5$H$^{6'}$) = 6.0, H$^1$ and H$^5$], 2.99 [1 H, dt, $J$(H$^1$H$^{6'}$) = $J$(H$^5$H$^{6'}$) = 6.0, $J$(H$^6$H$^{6'}$) = 15.3, H$^{6'}$] and 1.86 [1 H, d, $J$(H$^6$H$^{6'}$) = 15.3 Hz, H$^6$]. *m/z*: 453 ($M^+$, 23), 425 ([$M$ − CO]$^+$, 100) and 341 {[C$_6$H$_7$(PPh$_3$)]$^+$, 3%}.

**Dicarbonyl(η$^5$-2-methoxycyclohexadienyl)(triphenylphosphine)iron tetrafluoroborate 16.** This compound was prepared from **10** using a similar procedure to that described for the preparation of **15**. It was obtained as a pale yellow powder (1.27 g, 81%) after recrystallisation of the crude pale greenish yellow solid from dichloromethane–diethyl ether (Found: C, 56.8; H, 4.3. Calc. for C$_{27}$H$_{24}$BF$_4$FeO$_3$: C, 56.8; H, 4.2%). $\tilde{\nu}$(CO)(CH$_2$Cl$_2$)/cm$^{-1}$ 2046, 2004; Me(CN) 2045, 2002; (Nujol) 2045, 1985; $\delta_H$[(CD$_3$)$_2$CO] 7.21–7.60 (15 H, m, PPh$_3$), 6.95 [1 H, d, $J$(H$^3$H$^4$) = 6.0, H$^3$], 5.03 [1 H, t, $J$(H$^3$H$^4$) = $J$(H$^4$H$^5$) = 6.0, H$^4$], 3.70 (3 H, s, MeO), 3.23 [1 H, t, $J$(H$^4$H$^5$) = $J$(H$^5$H$^{6'}$) = 6.0, H$^5$], 2.96 [1 H, d, $J$(H$^1$H$^{6'}$) = 6.0, H$^1$], 1.99 [1 H, dt, $J$(H$^1$H$^{6'}$) = $J$(H$^5$H$^{6'}$) = 6.0, $J$(H$^6$H$^{6'}$) 9.2, H$^{6'}$] and 1.24 [1 H, d, $J$(H$^6$H$^{6'}$) = 9.2 Hz, H$^6$]; *m/z* 483 ($M^+$, 100), 455 ([$M$ − CO]$^+$, 30) and 371 {[MeOC$_6$H$_7$(PPh$_3$)]$^+$, 12%}.

**Dicarbonyl(η$^5$-cycloheptadienyl)(triphenylphosphine)iron tetrafluoroborate 17.** This compound was prepared from **11** using a similar procedure to that described for **15**. It was obtained as a light, orange-yellow powder (1.32 g, 78%) after recrystallisation of the crude orange oil from dichloromethane–diethyl ether. $\tilde{\nu}$(CO)(CH$_2$Cl$_2$)/cm$^{-1}$ 2045, 2004; (Nujol) 2040, 1989 [lit.,[14] $\tilde{\nu}$(CO)(MeCN)/cm$^{-1}$ 2049, 2008] The $^1$H NMR spectrum was similar to that reported (CD$_3$)$_2$CO.[17] $\delta_H$(CD$_3$CN) 7.50–7.78 (15 H, m, PPh$_3$), 6.90 [1 H, t, $J$(H$^2$H$^3$) = $J$(H$^3$H$^4$) = 6.3, H$^3$], 5.50 [2 H, t, $J$(H$^1$H$^2$) = $J$(H$^2$H$^3$) = $J$(H$^3$H$^4$) = $J$(H$^4$H$^5$) = 6.3, H$^2$ and H$^4$], 4.22 (2 H, br s, H$^1$ and H$^5$), 2.55 [2 H, dt, $J$(H$^6$H$^7$) = $J$(H$^{6'}$H$^{7'}$) = 3.6, $J$(H$^6$H$^{6'}$) = 10.2, H$^{6'}$ and H$^{7'}$] and 1.61 [2 H, d, $J$(H$^6$H$^{6'}$) = $J$(H$^7$H$^{7'}$) = 10.2 Hz, H$^6$ and H$^7$]. *m/z* 467 ($M^+$, 100), 439 ([$M$ − CO]$^+$, 30), 411 ([$M$ − 2CO]$^+$, 80) and 355 {[C$_7$H$_9$(PPh$_3$)]$^+$, 64%}.

### Polystyrene-supported complexes: typical procedure

A dark brown solution of dicarbonyl(η$^5$-cyclohexadienyl)iodoiron **9** (312 mg, 0.98 mmol) in dichloromethane (4 cm$^3$) was added to a solution of AgBF$_4$ (208 mg, 1.07 mmol) in acetone (20 cm$^3$) with stirring under dinitrogen. The resulting reddish brown mixture was stirred at room temperature for 15 min, and then filtered through a fritted disc into a suspension of polystyrene-supported triphenylphosphine (Aldrich, 304 mg) in acetone (20 cm$^3$). The orange-yellow mixture was stirred at room temperature under argon for 20 h, then filtered and the polymer product washed with dichloromethane and diethyl ether and dried under reduced pressure at 10 mmHg for *ca.* 30 min to give an orange-yellow powder (349 mg, 79%) (Found: Fe, 6.6. Calc. for [Fe(C$_6$H$_7$)(CO)$_2${PPh$_2$(C$_6$H$_4$CH-CH$_2$)}] **12**: Fe, 11.7%). $\tilde{\nu}$(CO)(Nujol)/cm$^{-1}$ 2045m, 1978s (br) and 1918 m.

### Treatment of crude polymer-supported iron complexes with trifluoroacetic acid

Trifluoroacetic acid (0.8 cm$^3$) was added dropwise to a suspension of the crude polymer product **12a** (110 mg) in dichloromethane (10 cm$^3$). The mixture was stirred at room temperature under argon for 15–30 min. then filtered and the polymer product washed with dichloromethane and diethyl ether and dried under reduced pressure at 10 mmHg for *ca.* 30 min. A light orange-yellow powder (101 mg, 92%) was obtained (Found: Fe, 5.6. Calc. for [Fe(C$_6$H$_7$)(CO)$_2${PPh$_2$-(C$_6$H$_4$CHCH$_2$)}]: Fe, 11.7%). $\tilde{\nu}$(CO)(Nujol)/cm$^{-1}$ 2045 and 1978.

### Treatment of crude polymer-supported iron complexes with [Ph$_3$C][BF$_4$]

A mixture of the crude polymer product **12a** (15 mg) and 5 molar equivalents of [Ph$_3$C][BF$_4$] in dichloromethane (3 cm$^3$) was refluxed for 1 h. The mixture was filtered, the polymer product washed with dichloromethane and diethyl ether and then dried under reduced pressure at 10 mmHg for *ca.* 30 min. A light orange-yellow powder (13 mg, 87%) was obtained (Found: Fe, 5.3. Calc. for [Fe(C$_6$H$_7$)(CO)$_2${PPh$_2$-(C$_6$H$_4$)(CHCH$_2$)}]: Fe, 11.7%). $\tilde{\nu}$(CO)(Nujol)/cm$^{-1}$ 2046s, 1979s and 1919w.

### Tricarbonyl[η$^4$-5-(triphenylphosphonio)cyclohexa-1,3-diene]-iron tetrafluoroborate 19

This known phosphonium adduct was prepared and purified using the procedure reported previously for a range of [Fe{η$^4$-C$_6$H$_7$(PR$_3$)}(CO)$_3$][BF$_4$] salts.[25] ṽ(CO)(CH$_2$Cl$_2$)/cm$^{-1}$ 2061, 1992; (MeCN) 2057 and 1986; δ$_H$(CD$_3$CN) 7.68–7.89 (15 H, m, PPh$_3$), 5.18 (1 H, m, H$_2$), 4.94 [1 H, t, *J*(H$^2$H$^3$) = *J*(H$^3$H$^4$) 6.0, H$^3$], 4.21 [1 H, ddd, *J*(H$^4$H$^{5'}$) = *J*(H$^{5'}$H$^6$) = 3.6, *J*(H$^{5'}$H$^{6'}$) = 10.4, H$^5$], 3.21 (1 H, m, H$^4$), 3.17 (1 H, m, H$^1$), 2.60 [1 H, ddd, *J*(H$^1$H$^{6'}$) = 3.6, *J*(H$^{5'}$H$^{6'}$) = 10.4, *J*(H$^6$H$^{6'}$) = 16.0, H$^{6'}$] and 1.89 [1 H, dd, *J*(H$^1$H$^6$) = 3.6, *J*(H$^6$H$^{6'}$) = 16.0 Hz, H$^6$]; δ$_C$(CD$_3$CN) 213.0 (CO), 139.1 (C), 135.3 (CH), 134.8 (CH), 130.2 (CH), 105.3 (CH), 86.0 (CH) 60.2 (CH), 54.2 (CH), 52.0 (CH) and 27.5 (CH$_2$); *m*/*z* 481 (*M*$^+$, 65) and 219 ([*M* − PPh$_3$]$^+$, 100%).

### Compound 20

A mixture of tricarbonyl(η$^5$-cyclohexadienyl)iron tetrafluoroborate **6** (205 mg, 0.67 mmol) and polystyrene-supported PPh$_3$ (Aldrich, 218 mg, 0.67 mmol PPh$_3$) in acetone (35 cm$^3$) was stirred at room temperature under nitrogen for 30 min. The polymer product was filtered off, rinsed with dichloromethane and diethyl ether, and then dried under reduced pressure at 10 mmHg for *ca.* 30 min. A dark orange powder (305 mg, 84%) was obtained. ṽ(CO)(Nujol)/cm$^{-1}$ 2052 and 1965.

### Tricarbonyl[η$^4$-5-(triphenylphosphonio)cyclohepta-1,3-diene]-iron tetrafluoroborate 21

This known phosphonium adduct was prepared and purified using the procedure previously reported for a range of [Fe{η$^4$-C$_7$H$_9$(PR$_3$)}(CO)$_3$][BF$_4$] salts.[26] ṽ(CO)(MeCN)/cm$^{-1}$ 2054, 1982; δ$_H$(CD$_3$CN) 7.71–7.89 (15 H, m, PPh$_3$), 5.27 [1 H, dd, *J*(H$^1$H$^2$) = *J*(H$^2$H$^3$) = 5.2, H$^2$], 4.98 [1 H, dt, *J*(H$^2$H$^3$) = *J*(H$^3$H$^4$) = 5.2, *J*(H$^1$H$^3$) = 0.8, H$^3$], 4.06 [1 H, dt, *J*(H$^3$H$^4$) = 5.2, *J*(H$^4$H$^{5'}$) = 2.8, H$^4$], 3.24 (1 H, m, H$^1$), 2.86 [1 H, dd, *J*(H$^4$H$^{5'}$) = 2.8, *J*(H$^{5'}$H$^{6'}$) = *J*(H$^3$H$^{5'}$) = 7.6 Hz, H$^{5'}$], 2.20 (2 H, m, H$^{6'}$ and H$^{7'}$), 1.84 (1 H, m, H$^6$) and 1.13 (1 H, m, H$^7$); δ$_C$(CD$_3$CN) 210.0 (CO), 135.0 (C), 133.1 (CH), 132.0 (CH), 130.1 (CH), 105.6 (CH), 91.5 (CH), 86.0 (CH), 58.0 (CH), 46.4 (CH), 34.6 (CH$_2$) and 28.0 (CH$_2$); *m*/*z* 588 (*M*$^+$, 35) and 326 ([*M* − PPh$_3$]$^+$, 100%).

### Dicarbonyl(triphenylphosphine)[η$^4$-5-(triphenylphosphonio)cyclohexa-1,3-diene]iron tetrafluoroborate 22

To a solution of dicarbonyl(η$^5$-cyclohexadienyl)(triphenylphosphine)iron tetrafluoroborate **15** (53 mg, 0.10 mmol) in acetone (10 cm$^3$) was added finely ground triphenylphosphine (30 mg, 0.11 mmol). The resulting solution was stirred at room temperature under argon for 15 min, followed by rotary evaporation to give compound **22** as a pale yellow oil (74 mg, 93%). ṽ(CO)(acetone)/cm$^{-1}$ 1984, 1928; (Nujol) 1979, 1919; δ$_H$[(CD$_3$)$_2$CO] 7.90–7.29 (30 H, m, 2PPh$_3$), 4.96 (1 H, m, H$^2$), 4.75 (1 H, m, H$^3$), 4.47 (1 H, m, H$^{5'}$), 2.68 (1 H, m, H$^4$), 2.53 (1 H, m, H$^1$), 2.42 (1 H, m, H$^{6'}$) and 1.96 [1 H, br d, *J*(H$^6$H$^{6'}$) 14.2 Hz, 1 H, H$^6$]; *m*/*z* 715 (*M*$^+$, 3) and 453 ([*M* − PPh$_3$]$^+$, 100%).

### Dicarbonyl[η$^4$-2-methoxy-5-(triphenylphosphonio)cyclohexa-1,3-diene](triphenylphosphine)iron tetrafluoroborate 23

This compound was prepared from dicarbonyl(η$^5$-2-methoxycyclohexadienyl)(triphenylphosphine)iron tetrafluoroborate **16** (133 mg) using a similar procedure to that used for the preparation of **22** above. It was obtained as a light greenish yellow oil (178 mg, 92%). ṽ(CO)(MeCN)/cm$^{-1}$ 2044w, 1998 (sh), 1982s and 1922s; δ$_H$[(CD$_3$)$_2$CO] 7.88–7.28 (30 H, m, 2PPh$_3$), 5.26 (1 H, m, H$^3$), 3.98 (1 H, m, H$^1$), 3.76 (1 H, m, H$^{5'}$), 3.18 (1 H, m, H$^4$), 3.01 (3 H, s, MeO), 1.95 (1 H, m, H$^{6'}$) and 1.21 (1 H, m, H$^6$); *m*/*z* 483 ([*M* − PPh$_3$]$^+$, 100%).

### Nucleophilic addition of hydride to polymer-supported dicarbonyldienyliron complexes

To a suspension of the crude iron polymer **12a** (15 mg) in dichloromethane (1 cm$^3$) was added a solution of NaBH$_4$ (8 mg) in water (1 cm$^3$). The mixture was stirred at room temperature under argon for 30 min, and then filtered. The polymer product was rinsed with water, then dichloromethane and diethyl ether, and dried under reduced pressure (10 mmHg) for *ca.* 30 min. An orange-yellow powder **24** (Nu = H, *m* = 0) (11 mg, 73%) was obtained. ṽ(CO)(Nujol)/cm$^{-1}$ 1960 and 1905.

### Addition of phosphorus nucleophiles

To a suspension of the crude iron polymer **12a** (18 mg) in dichloromethane (2 cm$^3$) was added tributylphosphine (5 drops). The mixture was stirred at room temperature under argon for 10–15 min and then filtered. The polymer product was rinsed with dichloromethane and diethyl ether, and dried under reduced pressure (10 mmHg) for *ca* 30 min. An orange-yellow powder **24** (Nu = PBu$_3$, *m* = 1) (27 mg, 83%) was obtained. ṽ(CO)(Nujol)/cm$^{-1}$ 1975 and 1920.

### Regeneration of polymer-supported dienyliron complexes

To a suspension of the dieneiron polymer product **25** (15 mg) in dichloromethane (2 cm$^3$) was added trifluoroacetic acid (*ca* 0.1 cm$^3$). The mixture was stirred at room temperature under argon for 15 min and then filtered. The polymer product was rinsed with water, dichloromethane and diethyl ether, and dried under reduced pressure (10 mmHg) for *ca.* 30 min.

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