

Preliminary communication

 New examples of Arbuzov rearrangements of coordinated phosphites initiated by metal-centred radicals ¹

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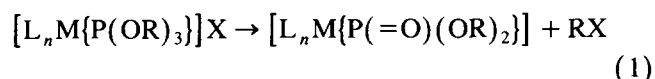
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Abstract

Reaction of the persistent, iron-centred radical $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2\cdot$ with tertiary phosphites $\text{P}(\text{OR})_3$ ($\text{R} = \text{Me}, \text{Et}$) results in the formation of the Arbuzov rearrangement products $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2\text{R}$, $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2\{\text{PO}(\text{OR})_2\}$ and $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{P}(\text{OR})_3\}\{\text{PO}(\text{OR})_2\}$. For both phosphites, the metal-centred radicals $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{P}(\text{OR})_3\}\cdot$ appear to be intermediates in a process which involves initial, direct abstraction by $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2\cdot$ of an alkyl group R from the coordinated $\text{P}(\text{OR})_3$ of $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{P}(\text{OR})_3\}\cdot$, followed by interception of the 16-electron intermediate, $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{PO}(\text{OR})_2\}$, by CO and $\text{P}(\text{OR})_3$.

Keywords: Iron; Chromium; Free radicals; Phosphites; Arbuzov reaction; 17-Electron compounds

A common reaction of coordination complexes containing trialkyl phosphites $\text{P}(\text{OR})_3$ bound to electrophilic metal ions is the so-called Arbuzov dealkylation reaction, in which a halide ion induced rearrangement proceeds as in Eq. (1) [1].

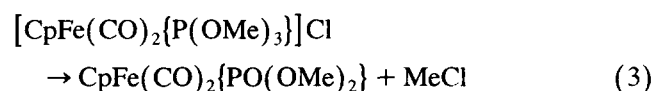
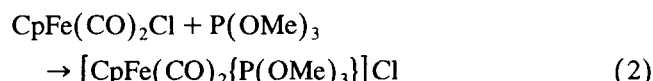


where M = transition metal; L = other ligands; R = alkyl groups; X = halide.

The reaction involves nucleophilic displacement of the neutral $\text{L}_n\text{M}\{\text{PO}(\text{OR})_2\}$ moiety from C-1 of the phosphite, which has been activated with respect to this process by the metal ion, to give a complex of the phosphorus(V) ligand $\{\text{PO}(\text{OR})_2\}^-$. Similar activation occurs on quaternisation of phosphites by alkyl halides [1].

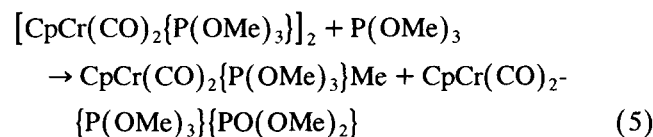
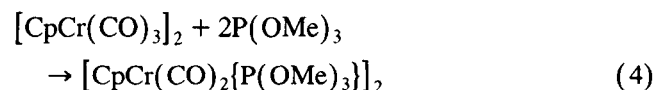
Relevant to this investigation, the reactions of $\text{CpFe}(\text{CO})_2\text{Cl}$ with a variety of phosphites have been studied in order to gain a better understanding of the

Arbuzov reaction. For example, reaction with $\text{P}(\text{OMe})_3$ was found to give initially the complex $[\text{CpFe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}]\text{Cl}$ (Eq. (2)), which reacted further to give the neutral complex $\text{CpFe}(\text{CO})_2\{\text{PO}(\text{OMe})_2\}$ [2a] and MeCl , as in Eq. (3).



Similarly, reaction of $(\eta^5\text{-C}_5\text{Ph}_5)\text{Fe}(\text{CO})_2\text{Br}$ with $\text{P}(\text{OMe})_3$ yielded the phosphonate compound $(\eta^5\text{-C}_5\text{Ph}_5)\text{Fe}(\text{CO})_2\{\text{PO}(\text{OMe})_2\}$ [2b].

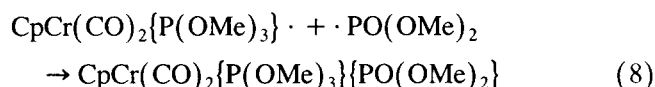
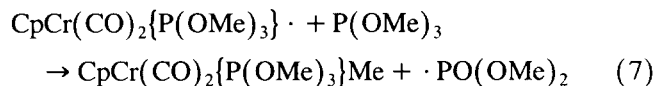
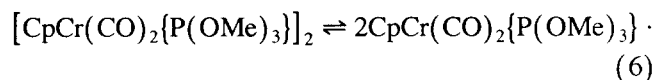
Far rarer are Arbuzov-like processes which proceed via radical mechanisms [1], especially reactions involving metal-centred radicals [1]. As an example, it has been reported that reaction of $[\text{CpCr}(\text{CO})_3]_2$ with $\text{P}(\text{OMe})_3$ proceeds as in Eqs. (4) and (5) [3].



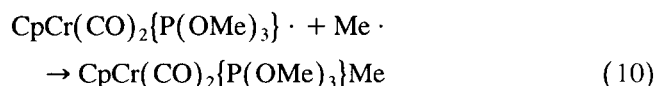
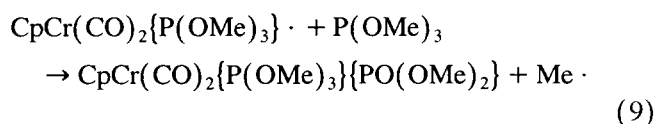
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¹ Dedicated to Professor Marvin Rausch on the occasion of his 65th birthday.

Both $[\text{CpCr}(\text{CO})_3]_2$ [4] and $[\text{CpCr}(\text{CO})_2\{\text{P}(\text{OMe})_3\}]_2$ [3,4e] dissociate extensively in solution to the corresponding 17-electron monomers, as indicated in Eq. (6) for the latter, and a mechanism involving metal-centred radicals has been proposed for the rearrangement (Eqs. (6)–(8)) [3].

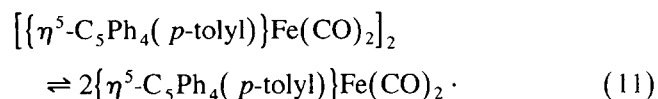


This mechanism has since been modified to bring it “in line with the products often encountered when radicals and alkyl phosphites react” (Eqs. (9) and (10)) [1].



It is possible that similar reactions of $[\text{CpFe}(\text{CO})_2]_2$ with trialkylphosphites $\text{P}(\text{OR})_3$ under forcing conditions (refluxing xylene) also give the apparent Arbusov products $\text{CpFe}(\text{CO})\{\text{P}(\text{OR})_3\}\{\text{PO}(\text{OR})_2\}$ and $\text{CpFe}(\text{CO})\{\text{P}(\text{OR})_3\}(\text{COR})$ [2c]. These reactions are believed to involve $\text{CpFe}(\text{CO})_2$ radical intermediates arising from thermal homolysis of $[\text{CpFe}(\text{CO})_2]_2$, although a variety of mechanisms could in fact pertain at the high temperature involved. Apparent Arbusov rearrangements have also been observed in reactions of $\text{CpFe}(\text{CO})_2((\eta^1\text{-Cp})$ [2d,e] and $\text{CpFe}((\eta^6\text{-toluene})$ [2f] with $\text{P}(\text{OMe})_3$. While the mechanisms of these reactions also remain speculative, iron-centred radicals are again implicated.

We have been investigating the chemistry of the iron-centred radical $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2 \cdot$, formed as in Eq. (11) [5].



While attempting to synthesize persistent substituted radical species by CO substitution reactions with bulkier ligands, we have found that the reaction of $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2 \cdot$ with $\text{P}(\text{OMe})_3$ at ambient temperature yields a mixture of three major products, $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2\text{Me}$ (**A**), $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2\{\text{PO}(\text{OMe})_2\}$ (**B**) and $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}\{\text{PO}(\text{OMe})_2\}$ (**C**), as well as minor, as yet unidentified, products. Although the products

cannot be readily isolated and thus have not yet been characterised by elemental analyses, they have all been identified unambiguously utilising spectroscopic techniques. This system thus represents a very rare example of an Arbusov rearrangement which is effected by a persistent metal-centred radical under mild conditions. We are therefore investigating in detail the effects of changing the nature of the phosphite, the solvent and the temperature, etc., and we report herein our initial results.

Treatment of a dark green suspension of $[\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2]_2$ in benzene at room temperature with slightly more than two molar equivalents of $\text{P}(\text{OMe})_3$ results in the formation of a yellow solution within approx. 30 min. Monitoring the reaction by IR spectroscopy showed that the carbonyl stretching bands [5] of the dimer at 1954 and 1780 cm^{-1} and of the monomer, $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2$, at 1989 and 1920 cm^{-1} were replaced by strong bands at 2000 and 1946 cm^{-1} , attributable to **A** [5], and at 2027 and 1981 cm^{-1} , attributable to **B** [2b]. No distinct absorption attributable to **C** was observed, but it should occur some 10–15 cm^{-1} lower [5] than for the Cp analogue (1967 cm^{-1}) [2c] and is likely obscured by the band of **A** at 1946 cm^{-1} . Interestingly, a peak appearing temporarily at 1897 cm^{-1} is probably attributable to $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\} \cdot$, the substituted iron-centred radical which we had initially hoped to isolate. It is, instead, an apparent intermediate en route to the Arbusov products.

The ^{31}P NMR (C_6D_6) spectrum of the reaction mixture exhibited a strong singlet at δ 103.8, attributable to **B** [2b], and a weaker doublet of doublets (AB quartet) at δ 116.7 and 170.8 (J_{pp} 155 Hz), attributable to the phosphonate and phosphite ligands, respectively, of **C** [1] and in good agreement with the corresponding data for the Cp analogue [2c]. The ^1H NMR spectrum of the reaction mixture exhibited, as well as $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}$ resonances at approx. δ 1.9 (Me) and in the phenyl region, a singlet at δ 1.07 (Fe–Me of **A**), a doublet at δ 3.64 (J_{HP} = 11 Hz; O–Me of **B**), a doublet at δ 3.42 (J_{HP} = 10 Hz; phosphite OMe of **C**) and doublets at δ 3.56 and 3.77 (J_{HP} = 11, 10 Hz, respectively diastereotopic phosphonate OMe of **C**).

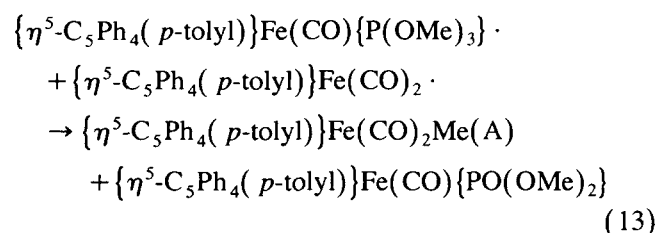
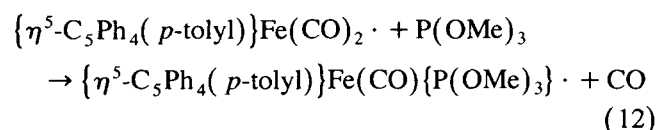
In an effort to ascertain the generality of the reactions of $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2$ with trialkyl- and triarylphosphites, we have also treated $[\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2]_2$ with $\text{P}(\text{OEt})_3$, $\text{P}(\text{O}^i\text{Pr})_3$ and $\text{P}(\text{OPh})_3$. Interestingly, the reaction of $\text{P}(\text{OEt})_3$ resulted in the slow formation of minor amounts of the Arbusov products $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2\text{Et}$ ($\nu(\text{CO})$ 1994, 1941 cm^{-1}), $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2\{\text{PO}(\text{OEt})_2\}$ ($\nu(\text{CO})$

¹ Compare $\text{CpFe}(\text{CO})\{\text{P}(\text{OMe})_3\}$, $\nu(\text{CO})$ at 1907 cm^{-1} in n-heptane [6].

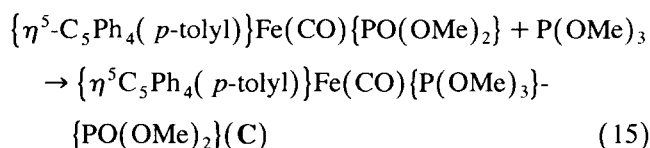
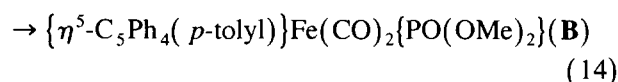
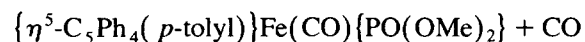
2025, 1980 cm^{-1}) and $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{P}(\text{OEt})_3\}\{\text{PO}(\text{OEt})_2\}$ (^{31}P NMR δ 112.4, 163.8; J_{PP} = 155 Hz). In this case, the dominant peak in the IR spectrum was at 1894 cm^{-1} ; unlike the corresponding peak at 1897 cm^{-1} in the $\text{P}(\text{OMe})_3$ system, the peak at 1894 cm^{-1} remained for at least 8 h.

Insignificant amounts of possible Arbusov products were found in reactions with $\text{P}(\text{O}^i\text{Pr})_3$ and $\text{P}(\text{OPh})_3$. The former reacted very slowly with $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2$, the IR spectra of reaction mixtures after 8 h exhibiting a carbonyl stretching band at 1886 cm^{-1} , which may be attributable to the 17-electron species $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{P}(\text{O}^i\text{Pr})_3\}$. Heating a mixture of $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2$ and $\text{P}(\text{OPh})_3$ to $\sim 70^\circ\text{C}$ for 15 min resulted in the growth only of a single peak at 1916 cm^{-1} , which may be attributed to the species $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{P}(\text{OPh})_3\}$. The presumed iron-centred radicals, $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{P}(\text{OR})_3\} \cdot$ ($\text{R} = \text{Me}, \text{Et}, ^i\text{Pr}, \text{Ph}$), are being investigated further and will be discussed elsewhere.

The relative proclivities of the phosphites to undergo Arbusov rearrangements in this system, i.e. $\text{P}(\text{OMe})_3 >> \text{P}(\text{OEt})_3 >> \text{P}(\text{O}^i\text{Pr})_3 \sim \text{P}(\text{OPh})_3$, parallels the trends of the ionic rearrangements shown in Eq. (1). In the latter cases, the reactions involve rate-determining nucleophilic attack on C-1 of the phosphites coordinated to, and hence activated by, an electrophilic metal ion, and thus the relative rates correlate well with the ease of nucleophilic attack on R [1], i.e. $\text{Me} > \text{Et} > ^i\text{Pr} > \text{Ph}$. A similar rationale seems appropriate here, and formation of the major products seems best explained by a mechanism involving initial, direct abstraction of alkyl groups R by $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})_2 \cdot$ from the coordinated $\text{P}(\text{OR})_3$ of the intermediates $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{P}(\text{OR})_3\} \cdot$ (Eqs. (12) and (13)).



The two phosphonate products are then the probable products of reactions of the 16-electron intermediate, $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{PO}(\text{OMe})_2\}$, with CO and $\text{P}(\text{OMe})_3$, respectively (Eq. (14) and (15)).



While the evidence for the key step being as shown in Eq. (13) is as yet largely circumstantial, the two alternatives which have been proposed elsewhere for the similar chromium system (Eqs. (6)–(10)) seem much less appropriate since they would involve either abstraction of a methyl group from an unactivated molecule of $\text{P}(\text{OMe})_3$ by a metal-centred radical, or, apparently, coordination of $\text{P}(\text{OMe})_3$ to the sterically very hindered, 17-electron compound $\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-tolyl})\}\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}$, followed by loss of methyl radical. Neither seems likely, and it is unfortunate that reactions of $[\text{CpCr}(\text{CO})_3]_2$ with other phosphites have not yet been investigated.

Acknowledgements

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