Preparation and Electrochemical Studies of the Compounds η^5-$C_5H_5RuCOLR$ (L = CO, PPh_3)

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There are numerous data available to suggest that cleavage of the iron–carbon σ bonds of compounds of the type η^5-$C_5H_5FeCOLR$ (R = alkyl, benzyl; L = CO, tertiary phosphine) by electrophilic reagents EX (X = halogen; E = H, X, HgX, CuX) proceeds via oxidative attack at the iron [1–6]. While intermediate oxidized iron species cannot easily be detected, there is both chemical and electrochemical evidence for both one- and two-electron pathways, *i.e.*

$$\begin{tikzcd}
 & {[\eta^5\text{-}C_5H_5FeCOLR]^+EX^-} \arrow[dr] & & \\
\eta^5\text{-}C_5H_5FeCOLR + EX \arrow[ur] \arrow[dr] & & \text{Products} \arrow[r] & (1) \\
 & {[\eta^5\text{-}C_5H_5FeCOLRE]^+X^-} \arrow[ur] & &
\end{tikzcd}$$

We have previously studied the seventeen electron species $[\eta^5\text{-}C_5H_5Fe(CO)_2CH_2Ph]^+$, which is a transient intermediate formed from η^5-C_5H_5-$Fe(CO)_2CH_2Ph$ in an electrochemically irreversible process (triangular-wave voltammetry) [2–4]. Wishing to form similar, more stable seventeen electron species in order to study their chemistry, we have begun working with ruthenium compounds of the type η^5-$C_5H_5Ru(CO)_2R$ and with substituted compounds of the type η^5-C_5H_5MCOLR (M = Fe, Ru). An approach utilizing ruthenium compounds seemed reasonable because higher oxidation states are often more stable for compounds of the second and third row transition metals than for their first row analogues [7]. The more electron rich tertiary phosphine substituted compounds also seemed worthy of study because of their expectedly greater ease of oxidation; it had already been shown that the disubstituted, seventeen electron complex $[\eta^5\text{-}C_5H_5\text{-}Fe(diphos)Me]^+PF_6^-$ is isolable [8]. We now report preliminary results involving both new synthetic routes to the ruthenium compounds, and triangular wave voltammetry studies of the compounds η^5-$C_5H_5Ru(CO)_2Me$ (*1*) and η^5-$C_5H_5MCOPPh_3Me$ (M = Fe, (*2*); Ru, (*3*)).

We initially expected that a series of the desired alkylruthenium compounds would be readily prepared as in eqn. (2)

$$\underset{4}{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2} \xrightarrow[THF]{Na\text{–}Hg} \underset{5}{2Na[\eta^5\text{-}C_5H_5Ru(CO)_2]} \xrightarrow{2RX} 2\eta^5\text{-}C_5H_5Ru(CO)_2R \qquad (2)$$

However, we quickly confirmed reports [9, 10] that yields of the methyl, ethyl and especially the benzyl compounds are rather low by this route, major by-products being the dimer, *4*, and ruthenocene. The procedures of Howell and Rowan [11], involving treatment of *4* with trialkyl phosphites, was also found to be generally unsuitable.

We next attempted to produce the anion, *5*, by treating *4* with trialkylborohydride salts, a method developed by Gladysz *et al.* to produce carbonylate anions from other dimeric metal carbonyls [12]. Treatment of THF solutions of *4* with $M[HBEt_3]$ (M = Li, Na, K) (Aldrich), followed by the addition of methyl iodide or benzyl chloride, results in 30–40% yields of the desired alkylruthenium compounds, η^5-$C_5H_5Ru(CO)_2R$ (R = Me, $PhCH_2$)*. While we have not investigated the reaction mechanistically, the ^1H NMR spectrum of the solution containing the reduced dimer exhibits a sharp singlet at τ 14.0, indicative of a formyl group [13] (the cyclopentadienyl region was unfortunately obscured by solvent resonances). The benzyl compound (ν_{CO} = 2020, 1965 cm^{-1} (cyclohexane); δ_{Ph} = 7.13, $\delta_{C_5H_5}$ = 5.09, δ_{CH_2} = 2.96 ($CDCl_3$)) can be obtained in 30% yield, a decided improvement on that reported previously [10]. The procedure would appear to be generally useful and is quite facile. Work-up procedures involve removing volatile materials under vacuum, followed by extraction with low-boiling petroleum ether and elution through an alumina column to separate the alkyl compound from any remaining dimer (*4*). A further advantage over the sodium amalgam procedure is that ruthenoncene, which can be difficult to separate from the alkyl compounds by sublimation or column chromatography, is not formed.

We find that one or both carbon monoxide ligands of the ruthenium compounds can be substituted photochemically by tertiary phosphines. For

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*The best yields seem to be obtained using the potassium salt, suggesting that ion-pairing can affect the reactivity of the anion, *1*.

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TABLE I. Electrochemical Data.

Compound	$(E_p)_a/V$[a]	n[b]	Remarks[c]
1	+1.58	1	Irreversible
2	+0.60	1	Quasi-reversible
	+1.28	1	Irreversible
3	+1.02	1	Irreversible
	+1.86	1	Irreversible
6	+0.80	1	Near reversible, $\Delta E_p = 0.08$ V

[a] Triangular-wave voltammetry, gl C working electrode, Ag/AgCl/0.1 *M* aq KCl reference electrode, 0.1 V/s, anhydrous CH_2Cl_2, 0.1 *M* Bu_4NBF_4 electrolyte. [b] See ref. 16. [c] Criteria: Irreversible – no apparent cathode peak; quasi-reversible $(i_p)_a > (i_p)_c$; near reversible $(i_p)_a \sim (i_p)_c$.

instance, irradiation of a solution of *1* and PPh_3 (1:3 molar ratio) in petroleum ether (b.p. 30–60 °C) for two days results in about a 40% yield of *3*, as well as smaller amounts of the disubstituted compound, η^5-$CpRu(PPh_3)_2Me$ (*6*) [14]. Unreacted *1* can readily be recovered by column chromatography, and thus much higher yields can, in fact, be effected.

The preliminary electrochemical results are given in Table I. Solutions of ferrocene were also examined under equivalent conditions. This compound yields a reversible one electron charge transfer process, and comparison of the current peaks from the voltammetric experiments with this known allows estimation of the number of electrons (n) in the unknown processes. In every case, assuming diffusion control at the current peak (i_p) and allowing reasonable differences in diffusion coefficient (D)*, it appears that each of the individual charge transfer steps involves one electron.

The results show that electrochemical oxidation of *1* is irreversible, as it is for the iron analogue [2, 4]. In addition, and contrary to expectations, *1* is more difficult to oxidize than is η^5-$C_5H_5Fe(CO)_2Me$ ($(Ep)_a = 1.15$ V in comparable experiments). Interestingly, while we have earlier reported that oxidation of *2* is irreversible at low scan rates with relatively positive switching potential (0.05 V/s, $E_\lambda = +1.60$ V) we now find that operating at higher scan rates (0.5 V/s), or at low scan rates (0.05 V/s) but with a less positive switching potential ($E_\lambda = +0.80$ V), gives a quasi-reversible one-electron process. Scanning the electrode at low rates to the more positive potentials appears to lead to coating and deactivation of the electrode, probably by the products of the second charge transfer process.

As shown in Table I, the initial one-electron oxidation of *3* is irreversible, and both *2* and *3* show a peak for a second subsequent irreversible oxidation step, apparently involving an additional electron. In addition, the electron rich bisphosphine compound, *6*, underwent a near reversible one electron charge transfer at significantly less positive potentials. Thus while our expectation that the ruthenium system would prove more electrochemically interesting than the previously studied iron system has led to some disappointment, studies of the phosphine substituted iron and ruthenium compounds are proving to be quite rewarding. Further coulometric and chemical experiments are being carried out in order to better understand the properties of the new seventeen and (possibly) sixteen electron species.

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*Calculations of n were made assuming that i_p is proportional to $D^{1/2}$. Molecular weights and relative values of $(i_p)_a$ were: ferrocene (MW 186), 1.0 (ref.); *1* (MW 237), 1.0; *2* (MW 502), 0.60; *3* (MW 426), 0.55; *6* (MW 705), 0.52.