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HYDROGEN ABSTRACTION AND DIMERISATION REACTIONS OF SOME ORGANO-TRANSITION METAL FREE RADICALS

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Summary

The 17-electron species $[M(CO)_{5-x}L_x]$ ($M = Mn, Re, x = 0$; $M = Mn, Re$; $L = Ph_3P, x = 1, 2$; $M = Mn, Re$; $L = (o-MeC_6H_4O)_3P, x = 2$; $M = Mn$; $L = (p-ClC_6H_4O)_3P, (PhO)_3P, x = 2$; $M = Mn$; $L = P(OMe)_3, x = 3$) have been generated by one electron oxidation of the corresponding anions and show typical radical reactivity, undergoing dimerisation or hydride abstraction in reactions controlled by steric effects. Evidence is presented for the source of the hydrogen atom. The 19-electron species $[M(CO)_3(\eta^7-C_7H_7)]^+$ ($M = Cr, Mo$) and $[Fe(CO)_3(\eta^5-C_5H_7)]^+$, generated by reduction of the corresponding cations, undergo dimerisation at the organic ligand. Similar treatment of $[Fe(CO)_2-L(\eta-cp)]^+$ ($L = CO, PPh_3, P(OPh)_3, Me_2CO$) yields $[Fe_2(CO)_4(\eta-cp)_2]$ and these reduction reactions are rationalised in terms of the nature of the HOMO in the intermediate radical. Similar reduction of $[Rh(diphos)_2]^+$ yield the 17-electron intermediate $[Rh(diphos)_2]$ and this also undergoes hydrogen abstraction.

We have previously reported on reactions of $[Re_2(CO)_{10}]$ with various organo-phosphanes and phosphites which, depending on the ligand, may produce ligand-substituted dimers, ligand-substituted mononuclear hydrides and metalated species. In particular, PPh_3 in refluxing xylene yields a complex mixture of products including $[Re(CO)_4PPh_3]_2$, $[ReH(CO)_3(PPh_3)_2]$ and $[Re(CO)_3(PPh_3)(C_6H_4PPh_2)]$. The intermediacy of the 17-electron radical species, $[Re(CO)_4PPh_3]$ and $[Re(CO)_3PPh_3]_2$ was invoked to account for this reactivity [1,2].

In order to study the reactivity of such paramagnetic species under milder conditions, we have generated them by one-electron reduction of the respective

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cations and one-electron oxidation of the respective anions and report here the results of these investigations.

Results and discussion

The anions $[\text{M}(\text{CO})_5]^-$ ($\text{M} = \text{Mn}, \text{Re}$), generated by reduction of $[\text{M}_2(\text{CO})_{10}]$, $[\text{M}(\text{CO})_3\text{L}_2]^-$ ($\text{M} = \text{Mn}, \text{Re}, \text{L} = \text{Ph}_3\text{P}, (o\text{-MeC}_6\text{H}_4\text{O})_3\text{P}$; $\text{M} = \text{Mn}, \text{L} = (p\text{-ClC}_6\text{H}_4\text{O})_3\text{P}, (\text{PhO})_3\text{P}$), $[\text{M}(\text{CO})_4\text{L}]^-$ ($\text{M} = \text{Mn}, \text{Re}, \text{L} = \text{PPh}_3$) and $[\text{Mn}(\text{CO})_2\text{-}\{\text{P}(\text{OMe})_3\}_3]^-$, all generated by reduction of the corresponding bromides [3], were subjected to one-electron oxidation by reaction with tropylium hexafluorophosphate. For reasons of solubility, reactions were carried in the polar solvents, methanol and tetrahydrofuran. Each reaction gave a single organometallic product. In the case of $[\text{M}(\text{CO})_4\text{L}]^-$ ($\text{M} = \text{Mn}, \text{Re}, \text{L} = \text{CO}, \text{PPh}_3$), the respective dimer was obtained in good yield. The bis-triphenylphosphane substituted dimers both had the 1,2-diaxial configuration [1,4]. In the case of all the more highly substituted anions, the corresponding hydrides were isolated, all adopting the *mer-trans* form [1,2,5]. It thus appears that the reactivity of the 17-electron radicals $[\text{M}(\text{CO})_x\text{L}_{5-x}]$ is controlled by steric factors, in that the presence of two or more phosphorus donor ligands prevents dimerisation, allowing the radicals to undergo hydrogen abstraction reactions with the solvent.

The *mer-trans* configuration of the hydrides is in accord with expectations. Thus, if the $[\text{M}(\text{CO})_3\text{L}_2]$ radicals adopt a square pyramidal coordination geometry with the phosphorus donor ligands in mutually *trans* positions analogous to that reported for $[\text{Mn}(\text{CO})_3(\text{PBu}_3)_2]$ [6], then the unpaired electron can be envisaged as occupying the sixth site and hydrogen abstraction will yield the observed isomer.

A similar argument applied to the $[\text{M}(\text{CO})_4\text{L}]$ radicals, which would also be expected to have L in the basal plane and the unpaired electron trans to the axial carbonyl group, would suggest coupling should lead to production of a 1,2-diequatorial isomer, whereas the 1,2-diaxial form is obtained. It is relevant that reaction of a bulky ligand such as PPh_3 with $[\text{M}_2(\text{CO})_{10}]$ ($\text{M} = \text{Mn}$ or Re) [1] leads to formation of only the diaxial disubstituted isomer and here steric interactions presumably mitigate against formation of the diequatorial form. Similar steric repulsions would presumably arise in the interaction of two $[\text{M}(\text{CO})_4\text{L}]$ radicals and as it is likely that such species would be fluxional it is possible that steric constraints induce rearrangement prior to bond formation.

The isolation of hydrides from reaction of $[\text{M}(\text{CO})_3\{(o\text{-MeC}_6\text{H}_4)_3\text{P}\}_2]$ was unexpected, as we have previously reported that the only mononuclear product obtained in the high temperature reaction of $[\text{Re}_2(\text{CO})_{10}]$ and $(o\text{-MeC}_6\text{H}_4\text{O})_3\text{-P}(\text{L})$ was the metalated species, $[\text{Re}(\text{CO})_3\text{L}(\text{L}-\text{H})]$ [2]. In view of this discrepancy we have re-examined this reaction performed under the conditions reported earlier and now believe our earlier findings to be incorrect. Thus, we have confirmed the presence of 1,2-diaxial- $[\text{Re}_2(\text{CO})_8\text{L}_2]$, from a 16 h reaction but believe the compound from a longer reaction identified as $[\text{Re}(\text{CO})_3\text{L}(\text{L}-\text{H})]$ to, in fact, be $[\text{ReH}(\text{CO})_3\{(o\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}\}_2]$.

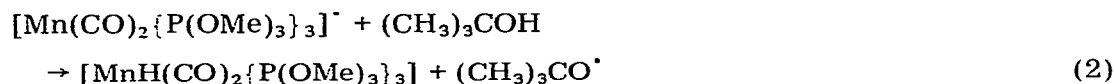
In order to investigate the details of hydrogen abstraction, we carried out the oxidation of $[\text{Mn}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]^-$ in methanol and its deuterated analogues. Reactions in both methanol- d_4 and in CD_3OH gave solely the deuteride, $[\text{MnD}-$

$(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3$], thereby indicating that only methyl hydrogen atoms are involved in the abstraction process in this solvent. This α -abstraction is similar to that observed in the case of formation of $[\text{Ir}(\text{H})\text{Cl}_2(\text{PPh}_3)_3]$ in alcoholic solvents, although in that case there was no indication that the reaction followed a free radical pathway [7]. Such α -hydrogen abstraction is well known in the reaction of organic free radicals with primary alcohols and the hydroxymethyl radical so formed is known to undergo disproportionation (equation 1).



In this study we experienced great difficulty in unequivocally characterising formaldehyde produced by such a reaction. However, similar oxidation of $[\text{Mn}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]^-$ in propan-1-ol gave the expected hydride. Propanal was the only organic material, besides the alcohol and a small amount of $\text{P}(\text{OMe})_3$, identified by GLC.

That these metal-centred radicals are capable of abstracting hydrogen atoms from hydroxyl groups was demonstrated by oxidation of $[\text{Mn}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]^-$ in *t*-butanol. Again the sole metal-containing product was the corresponding hydride, but in this case production of acetone was confirmed by GLC (equations 2 and 3) [8].



In our previous study [1] we were unable to unequivocally confirm the source of hydrogen in the reaction of $[\text{Re}_2(\text{CO})_{10}]$ and PPh_3 in xylene [1]. However, we now report that when these reagents are heated in toluene in a sealed tube at 120°C overnight, $[\text{ReH}(\text{CO})_3(\text{PPh}_3)_2]$ was identified as the main metal-containing product (IR and NMR) and the production of 1,2-diphenylethane was confirmed by GLC.

The above reactions all involve a 17-electron intermediate formed by oxidation of an 18-electron anion. We have also examined one-electron reduction of some 18-electron organometallic cations, in which the initial product will have a 19-electron configuration. Such reactions have been reported previously [9]. However, in view of the above results we believed a brief re-examination was merited in order to ascertain if any metal hydrides were formed.

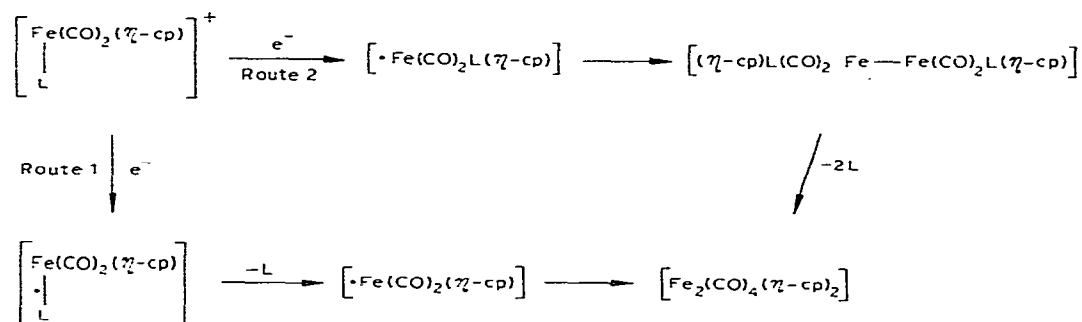
Reduction of $[\text{Fe}(\text{CO})_2\text{L}(\eta\text{-cp})]^+$ ($\text{L} = \text{CO}, \text{PPh}_3, \text{P}(\text{OPh})_3, \text{Me}_2\text{CO}$) by a variety of agents (zinc-copper couple, sodium amalgam and chromous ion) in acetone led to $[\text{Fe}_2(\text{CO})_4(\eta\text{-cp})_2]$ in all cases. Similar treatment of the tropylium containing cations, $[\text{M}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$ ($\text{M} = \text{Cr}, \text{Mo}$) and the cyclohexadienyl containing cation, $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_7)]^+$ with chromous ion in acetone yielded solely the ligand-coupled products $[(\text{OC})_3\text{M}(\eta^6\text{-C}_7\text{H}_7\text{-}\eta^6\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3]$ and $[(\text{OC})_3\text{Fe}(\eta^4\text{-C}_6\text{H}_7\text{-}\eta^4\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3]$. There was no evidence for metal hydride formation in any of these reactions or any evidence for hydrogen abstraction onto the organic ligands to form cyclopentadiene, cycloheptatriene and cyclohexadiene complexes respectively.

The NMR spectra of $[(\text{OC})_3\text{M}(\eta^6\text{-C}_7\text{H}_7\text{-}\eta^6\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3]$ and $[(\text{OC})_3\text{Fe}(\eta^4\text{-C}_6\text{H}_7\text{-}\eta^4\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3]$ are complex and the spin-spin coupling patterns are

not clearly resolved. It was not, therefore, possible to make a detailed analysis of the stereochemistry at the bridging carbon atoms of each molecule in a manner similar to that used by Pauson et al. of distinguishing *exo* and *endo* isomers in $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_7\text{R})]$ [10].

The nature of the products formed from these 19-electron radical intermediates thus suggest a marked dependence on the nature of the HOMO in the radical. Coupling at the organic ligand, indicates that the HOMO in $[\text{M}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]$ and $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_7)]$ is ligand based, whereas in $[\text{Fe}(\text{CO})_3(\eta\text{-cp})]$ it is either metal based or has Fe—CO antibonding character. This would allow coupling by either of the two routes outlined in Scheme 1, which cannot

SCHEME 1



easily be distinguished. However, the LUMO in the analogous complex $[\text{Mn}(\text{CO})_3(\eta\text{-cp})]$ is of M—CO antibonding character [11] and as this would be the HOMO in the 19-electron iron analogue we suggest coupling occurs via route 1. If there is a choice of η^1 -ligands that may be lost in this process then it is that the most weakly bound is displaced [12]. Others have also observed that the 19-electron species, $[\text{Ni}(\text{PPh}_3)_2(\eta\text{-cp})]$ also undergo a rapid loss of PPh_3 , followed by further reaction of the 17-electron product [13].

17-electron radicals can also be generated by one-electron reduction of 16-electron cations and, accordingly, we have found that treatment of $[\text{Rh}(\text{diphos})_2]^+$ with sodium amalgam in methanol leads to isolation of $[\text{RhH}(\text{diphos})_2]$, presumably formed by reaction of the intermediate $[\text{Rh}(\text{diphos})_2]$ radical with the solvent. Others have reported similar findings for this radical generated by electrochemical means [14]. Attempts to perform similar reductions of $[\text{Rh}(\text{PPh}_3)_2\text{L}]^+$ (L = cycloocta-1,5-diene, norbornadiene) led to total decomposition of the complexes.

Experimental

All reactions were performed under an atmosphere of dry oxygen-free nitrogen. All solvents and reagents were purified by standard techniques before use and all solvents were thoroughly degassed by three freeze-pump-thaw cycles immediately prior to use. Transfer of solvents between vessels and all other manipulations were carried out with the rigorous exclusion of air.

Mass spectra were obtained on an AEI MS9 spectrometer. Infrared spectra

were recorded on a Perkin—Elmer 457 spectrometer. NMR spectra were recorded on a Perkin—Elmer R32 spectrometer.

The anions $[M(CO)_5]^-$ ($M = Mn, Re$), were prepared by treatment of $M_2(CO)_{10}$ with sodium amalgam. Other anions were prepared by treating the corresponding bromides $[(M(CO)_{5-n}L_nBr)]$ with sodium amalgam [3]. A typical procedure for subsequent oxidation of these anions is illustrated below.

Oxidation of $[Re(CO)_5]^-$

A solution of $[Re(CO)_5]^-$ in THF (10 ml), prepared by reacting $[Re_2(CO)_{10}]$ (1.37 g, 0.2 mmol) with sodium amalgam, was treated with tropylium hexafluorophosphate (0.1 g, 0.43 mmol) in THF (20 ml). The reaction mixture was stirred at room temperature for 2 h and then evaporated to dryness. The yellow solid was extracted with hot hexane (5×20 ml) and the combined extracts concentrated to give colourless crystals of $Re_2(CO)_{10}$ (81 mg, 59% yield).

In the case of the reactions yielding hydrides, concentration of the reaction mixture, produced the solid product. Spectroscopic parameters for characterisation of these hydrides are given in Table 1.

Reaction between $[Re_2(CO)_{10}]$ and tri(*o*-tolyl)phosphite

A mixture of $Re_2(CO)_{10}$ (0.5 g, 0.77 mmol) and tri(*o*-tolyl)phosphite (2.49 g, 7.1 mmol) was heated in xylene (25 ml) under reflux for 50 h. The solid was then removed under vacuum and the residue subjected to preparative TLC. $[ReH(CO)_3\{(O-CH_2C_6H_4O)_3P\}_2]$ was isolated as a colourless solid (spectroscopic data as in Table 1) and no other organometallic compound was obtained.

Reduction of $[M(CO)_3(\eta-C_7H_7)]PF_6$ ($M = Cr, Mo$) by chromium(II)

An aqueous solution of chromium(II) was prepared by treating $[CrCl_3 \cdot 6 H_2O]$ (3.57 g, 0.014 mol) with zinc (6.06 g, 0.091 g atom) and concentrated hydrochloric acid (8 ml) in water (10 ml). This sky-blue solution was then added to a

TABLE 1
SPECTROSCOPIC PARAMETERS FOR THE PRODUCTS OF ONE-ELECTRON OXIDATION REACTIONS

Complex	IR $\nu(CO)$ (cm^{-1})	NMR ^a	
		δ (ppm) ^b	J (Hz)
$[ReH(CO)_3(PPh_3)_2]$	1935	-4.0	18
$[MnH(CO)_3(PPh_3)_2]$	1920	-7.4	29
$[ReH(CO)_3\{(MeC_6H_4O)_3P\}_2]$	1965	-6.4	30
$[MnH(CO)_3\{(MeC_6H_4O)_3P\}_2]$	1960	-6.5	52
$[MnH(CO)_3\{(ClC_6H_4O)_3P\}_2]$	1950	-8.2	48
$[MnH(CO)_3\{(PhO)_3P\}_2]$	1960	-8.2	50
$[MnH(CO)_2\{(MeO)_3P\}_3]$	1950s, 1885s	-8.2	50, 80
$[Mn_2(CO)_8(PPh_3)_2]$	1980sh, 1955vs		
$[Re_2(CO)_8(PPh_3)_2]$	1960vs		

^a Metal hydride chemical shifts only reported. ^b Signals for all complexes $[MH(CO)_3L_2]$ were 1/2/1 triplets. Signal for $[MnH(CO)_2\{P(OMe)_3\}_3]$ was a doublet of triplets.

solution of the salt (approx. 1.5×10^{-3} mol) in a water/THF mixture (1/1 ratio, 20 ml) and the mixture stirred at room temperature for 30 min. After this time, the red precipitate was removed from the green supernatant liquid by filtration. Recrystallisation from chloroform gave small red needles $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_7)]_2$ (Yield 39%). Anal. Found: C, 52.88; H, 3.77; $\text{C}_{20}\text{H}_{14}\text{O}_6\text{Cr}_2$ calcd.: C, 52.86; H, 3.08%. Infrared spectrum, $\nu(\text{CO})$ 1982vs, 1924s, 1894s cm^{-1} . Mass spectrum, m/z 454, M^+ . NMR spectrum (CDCl_3), δ 5.95 ppm (m, 2H, H(3,4)), δ 4.77 ppm (m, 2H, H(2,5)), δ 3.27 ppm (m, 2H, H(1,6)), δ 1.23 ppm (m, 1H, H(7)). $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]_2$ (Yield 52.4%). Anal. Found: C, 44.18; H, 2.71; $\text{C}_{20}\text{H}_{14}\text{O}_6\text{Mo}_2$ calcd.: C, 44.29; H, 2.58%. Infrared spectrum, $\nu(\text{CO})$, 1990vs, 1930s, 1888s cm^{-1} . Mass spectrum, m/z , 546, M^+ . NMR spectrum ($\text{DMSO-}d_6$), δ 6.75 ppm (m, 2H, H(3,4)), δ 6.31 ppm (m, 2H, H(2,5)), δ 5.20 ppm (m, 2H, H(1,6)), δ 1.88 ppm (m, 1H, H(7)).

Reduction of $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_7)]\text{PF}_6$ by chromium(II)

A solution of $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_7)]\text{PF}_6$ (1.0 g, 0.0027 mol) in water (20 ml) was treated with aqueous chromium(II) solution prepared as detailed above. The mixture was warmed gently for 30 min and then filtered. The filtrate was extracted with ether (3×25 ml), the combined extracts dried and the ether removed under vacuum. The remaining yellow gum was chromatographed on a silica gel column (20 cm \times 2.5 cm) and a yellow band eluted with toluene/petrol (b.p. 80–100°C). (1/1 v/v ratio). The product was isolated as yellow plates. Yield 17% based on $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7)]_2$. Infrared spectrum, $\nu(\text{CO})$ 2030vs, 1970vs, br cm^{-1} . Mass spectrum, m/z 438, M^+ ; $M - n(\text{CO})^+$ ($n = 1-6$). NMR spectrum (CDCl_3), δ 5.21 ppm (m, 2H), δ 2.95 ppm (m, 2H), δ 1.10 ppm (m, 2H), δ 1.72 ppm (m, 1H). Anal. Found: C, 48.95, H, 2.51; $\text{C}_{18}\text{H}_{14}\text{O}_6\text{Fe}_2$ calcd.: C, 49.32; H, 3.20%.

Reduction of $[\text{Fe}(\text{CO})_2\text{L}(\eta\text{-cp})]\text{PF}_6$ ($\text{L} = \text{CO}, \text{PPh}_3, \text{P}(\text{O}Ph)_3, \text{Me}_2\text{CO}$)

Solutions of $[\text{Fe}(\text{CO})_2\text{L}(\eta\text{-cp})]\text{PF}_6$ in acetone were treated with sodium amalgam ($\text{L} = \text{P}(\text{O}Ph)_3$), chromium(II) solution ($\text{L} = \text{CO}$) or a zinc-copper couple ($\text{L} = \text{P}(\text{O}Ph)_3, \text{PPh}_3, \text{Me}_2\text{CO}$). In all cases the acetone solution became yellow-orange and appropriate work-up lead to isolation of $[\text{Fe}_2(\text{CO})_4(\eta\text{-cp})_2]$ in all cases ($\nu(\text{CO})$ 2001s, 1800s, 1785s cm^{-1} [15]).

Acknowledgments

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