Synthetic Applications of the Reaction of Silver(I) Salts with the Bis[dicarbonyl(π-cyclopentadienyl)iron] Complex

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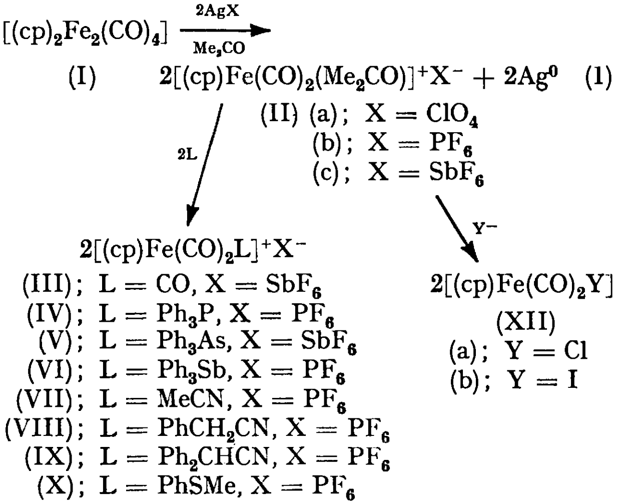
In polar solvents the iron–iron bond of the dimeric complex $[(cp)_2Fe_2(CO)_4]$ (cp = π-cyclopentadienyl) is smoothly oxidised by Ag^I ions to give diamagnetic cations containing a co-ordinated solvent molecule, and metallic silver. Using acetone as solvent, the cation $[(cp)Fe(CO)_2(acetone)]^+$ has been isolated and fully characterised as the hexafluorophosphate salt. The use of Ag^I salts as convenient reagents for the synthesis of a wide variety of $[(cp)Fe(CO)_2R]$ [R = NO_3, CF_3CO_2, SCN, NCO, $PhCO_2$, p-Me-$C_6H_4SO_3$, and $OP(O)(OPh)_2$], and $[(cp)Fe(CO)_2L]^+$ {L = CO, Ph_3P, Ph_3As, Ph_3Sb, MeCN, $PhCH_2CN$, Ph_2CHCN, PhSMe, and $[(cp)Fe(CO)_2I]$} complexes is described. Some mechanistic implications of the reaction are briefly discussed.

MUCH attention has recently centred on the oxidation of the iron–iron bond in the dimeric complex $[(cp)_2Fe_2(CO)_4]$ (I) (cp = π-cyclopentadienyl) and its derivatives.[1-4] Electrochemical oxidation has established that, for the ditertiary phosphine bridged complex[2] $[\{(cp)Fe(CO)\}_2\{Ph_2P(CH_2)_3PPh_2\}]$, an initial one-electron oxidation step gives a novel paramagnetic cation $[\{(cp)Fe(CO)\}_2\{Ph_2P(CH_2)_3PPh_2\}]^+$ involving a 'one-electron metal–metal bond.' A similar cation has been produced from the phosphine derivative *via* chemical oxidation with iodine, $AgClO_4$, or $AgSbF_6$[4] but the analogous cation derived from (I) has not been detected under similar conditions. However anhydrous iron(III) perchlorate reacts[3] with complex (I) to produce diamagnetic cations of the type $[(cp)Fe(CO)_2S]^+$ (S = solvent). Reaction of such complexes, generated *in situ*, with neutral or anionic ligands has proved to be a useful synthetic route for iron complexes of the type $[(cp)Fe(CO)_2L]^+$ or $[(cp)Fe(CO)_2R]$ respectively.[3] Apart from the work of Ruff[5] with Group VI metal decacarbonyl dianions, there has been little general synthetic exploitation of the oxidising power of silver(I) salts. We present here evidence that silver(I) salts are at least as useful synthetic reagents *vis à vis* complex (I) as iron(III) perchlorate, and in several cases have distinct advantages over the latter [equations (1) and (2)].



$$[(cp)_2Fe_2(CO)_4] \xrightarrow[\text{Me}_2\text{CO}]{2\text{AgX}} 2[(cp)Fe(CO)_2(Me_2CO)]^+X^- + 2Ag^0 \quad (1)$$

(I)

(II) (a); $X = ClO_4$
(b); $X = PF_6$
(c); $X = SbF_6$

$\xrightarrow{2L}$ $2[(cp)Fe(CO)_2L]^+X^-$
(III); L = CO, $X = SbF_6$
(IV); L = Ph_3P, $X = PF_6$
(V); L = Ph_3As, $X = SbF_6$
(VI); L = Ph_3Sb, $X = PF_6$
(VII); L = MeCN, $X = PF_6$
(VIII); L = $PhCH_2CN$, $X = PF_6$
(IX); L = Ph_2CHCN, $X = PF_6$
(X); L = PhSMe, $X = PF_6$
(XI); L = $[(cp)Fe(CO)_2I]$, $X = SbF_6$

$\xrightarrow{Y^-}$ $2[(cp)Fe(CO)_2Y]$
(XII)
(a); Y = Cl
(b); Y = I

$$[(cp)_2Fe_2(CO)_4] \xrightarrow[\text{Me}_2\text{CO}]{2\text{AgR}} 2[(cp)Fe(CO)_2R] + 2Ag^0 \quad (2)$$

(XIII); $R = NO_3$
(XIV); $R = CF_3CO_2$
(XV); R = SCN
(XVI); R = NCO
(XVII); $R = PhCO_2$
XVIII); R = p-Me-$C_6H_4SO_3$
(XIX); $R = OP(O)(OPh)_2$

RESULTS AND DISCUSSION

Addition of a soluble silver salt AgX ($X = ClO_4^-$, PF_6^-, or SbF_6^-) to an acetone solution of complex (I) resulted in rapid discharge of the maroon colour and its replacement by a deep red hue. The progress of the reaction was conveniently followed by monitoring the disappearance of the i.r. absorption below 2000 cm^{-1} characteristic of (I). Oxidation was essentially complete within a few minutes. Metallic silver was deposited as a silver mirror or, less commonly, as silver powder. Using silver(II) hexafluorophosphate or silver(I) hexafluoroantimonate(V) as oxidant, the reaction mixture could be worked up to yield red crystalline salts (IIb) and (IIc) which contained a co-ordinated acetone molecule. In the case of the hexafluorophosphate derivative, the salt has been fully characterised as the complex $[(cp)Fe(CO)_2(acetone)]^+PF_6^-$ (IIb). Microanalytical data (Table) are in agreement with this formulation and the n.m.r. spectrum (in acetone solution) shows, besides solvent absorptions, two resonances of relative area 5 : 6 corresponding to the cyclopentadienyl and acetone ligand protons respectively.

Complex (IIb) is stable for at least a day in dry air and even after several days decomposition is not extensive. Solutions of the complex appear to be rather less stable. The cation of (II) has been assumed to intervene in the oxidation of complex (I) using either electrochemical[1] means or iron(III) perchlorate,[3] but solid

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[1] J. A. Ferguson and T. J. Meyer, *Inorg. Chem.*, 1971, **10**, 1025.

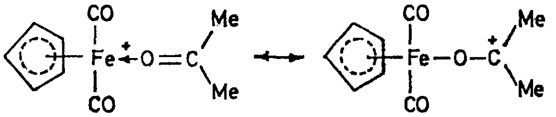
[2] J. A. Ferguson and T. J. Meyer, *Chem. Comm.*, 1971, 1544.

[3] E. C. Johnson, T. J. Meyer, and N. Winterton, *Inorg. Chem.*, 1971, **10**, 1673.

[4] R. J. Haines and A. L. du Preez, *Inorg. Chem.*, 1972, **11**, 330.

[5] W. J. Schlientz and J. K. Ruff, *Synthetic Inorg. Metal-Org. Chem.*, 1971, **1**, 215.

salts of the cation have not previously been characterised. Although Silverthorn[6] has recently characterised the related cation $[(cp)Fe(dmpe)(acetone)]^+$ [dmpe = 1,2-bis(dimethylphosphino)ethane], the stability of complex (IIb) is rather unexpected and may involve resonance with an oxo-carbenium canonical form [equation (3)].


(3)

Dilution of an acetone solution of complex (II) with acetone-d_6 resulted in a considerable reduction in intensity of the acetone ligand n.m.r. resonance. Similarly a solution of the solid complex in acetone-d_6 showed no resonance due to the complexed acetone molecule. Both observations indicate that the iron-bonded acetone molecule exchanges with solvent, but that this exchange is slow on the n.m.r. time-scale since resonances due to both co-ordinated and free solvent are observed in acetone solution.

Reactions in which the smooth oxidation of complex (I) by silver(I) salts was harnessed for synthetic purposes may be classified in three distinct groups as follows.

(*A*) *Reaction of Complex* (I) *with* AgX (X *is a Non-co-ordinating Anion*) *followed by Addition of a Neutral or Anionic Ligand*.—This route, which parallels the iron(III) perchlorate route of Meyer,[3] was used to synthesise a wide variety of iron complexes [(II)—(V) and (VII)—(XI)], some of which [(VII)—(X)] are reported for the first time. Under the appropriate conditions (*vide infra*), the reaction is rapid and yields are high (often 70—80%). In one case, the synthesis of the iodonium-bridged complex (XI), CH_2Cl_2 was successfully used as solvent. This simple route to this complex represents a useful addition to published synthetic procedures.[7] Rather disappointingly, the reaction of complex (IIb) with iodobenzene to give the asymmetric iodonium salt $[(cp)Fe(CO)_2\text{-I-Ph}]^+PF_6^-$ did not take place. Suitable silver(I) salts for procedure (A) are the perchlorate, hexafluorophosphate, or hexafluoroantimonate(V).

Despite the formal similarity with Meyer's use of iron(III) perchlorate,[3] the reaction of complex (I) with silver(I) perchlorate shows some significant differences. In contrast to Meyer's method, the present reaction is rapid only if the ligand is added *before* the oxidant and is otherwise quite slow. Thus in the oxidation of (I) with $AgClO_4$ or $AgPF_6$ the yellow colour and characteristic i.r. spectrum of the acetonitrile complex (VIII) appeared virtually instantaneously if the ligand was added before the oxidant. If acetonitrile was added after the silver(I) salt it was several hours before the presence of complex (VIII) could be detected. Simple competition between acetonitrile and the solvent for transient unsolvated $[(cp)Fe(CO)_2]^+$ is unlikely to be involved since the Fe^{III} oxidation is not similarly sensitive to reaction conditions. In the Ag^I-induced redox process the oxidant is cleanly removed from the reaction mixture as metallic silver. It seems reasonable to envisage that, in the absence of external ligand, the initially formed cation containing a co-ordinated solvent molecule could interact with perchlorate or hexafluorophosphate anions to form tightly bound ion-pairs. Slow reaction of either of these possible intermediates with the ligand would account for the slow formation of the ultimate product. When iron(III) is the oxidant, the iron(II) cation produced remains in solution and may reasonably be assumed to complete successfully for anions with the cation containing the co-ordinated solvent molecule, hence preventing formation of a relatively inert intermediate.

(*B*) *Reaction of Complex* (I) *with* AgR (R *is a Co-ordinating Anion*).—Several interesting complexes [(XIII)—(XIX)] have been prepared by this method. The novel *O*-bonded benzoato- (XVII), toluene-*p*-sulphonato- (XVIII), and diphenyl phosphato-complexes (XIX) are here reported for the first time and would probably be difficult to prepare by any other route. In the case of the known nitrato-complex (XIII), the yield by the present method is considerably better than that obtained in the previously reported synthesis.[3] The ready availability of the silver(I) nitrate oxidant should make the new route the method of choice. Use of silver(I) isocyanate makes available for the first time a simple one-step synthesis of the isocyanato-complex (XVI). Of all the complexes reported in this paper, the diphenyl phosphato-complex (XIX) alone did not survive recrystallisation and is characterised by its i.r. spectrum.

The only limitation to this versatile method would appear to be the solubility of the silver salt involved. Insolubility of the latter doubtless accounts for the failure of complex (I) to react with either silver(I) sulphate or silver(I) cyanide. While complex (I) reacts rapidly with silver(I) nitrite, the product was not the expected $[(cp)Fe(CO)_2ONO]$ complex. This anomalous reaction is currently under investigation.

(*C*) *Reaction of Ligand with Preformed Complex* (II) *in an Indifferent Solvent*.—The isolation and characterisation of the solid complex containing a co-ordinated solvent molecule makes it possible to enhance the reactivity of complex (II) by carrying out subsequent reactions with ligands in solvents of low co-ordinating ability. Thus the ligand Ph_3Sb, which fails to react with (II) according to procedure (A), gives the complex (VI) in 40% yield when reacted with (II) in methylene chloride. This route promises to be of particular use for ligands of low reactivity. On treatment with nitrogen, Silverthorn's complex[5] $[(cp)Fe(dmpe)(acetone)]^+$ gives the novel dimeric μ_2-dinitrogen-cation $[(cp)_2Fe_2(dmpe)_2N_2]^+$. When the complex (IIb) was shaken for several hours in CH_2Cl_2 solution under an atmosphere of nitrogen gas (25 p.s.i.), a red oil was recovered which appeared to contain some (*ca.* 2%)

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[6] W. E. Silverthorn, *Chem. Comm.*, 1971, 1310.

[7] R. J. Haines and A. L. du Preez, *J. Chem. Soc.* (*A*), 1970, 2341 and references therein.

nitrogen; however, no characterisable products could be isolated.

Some preliminary experiments were carried out to extend this synthetic route to other oxidants and metal–metal bonded systems. Thus complex (I) reacts with tris(*p*-bromophenyl)amminium hexachloroantimonate[8] to give a 30% yield of the chloro-complex (XIIa). The chlorine atom of the latter presumably originates in the $SbCl_6^-$ anion[9] but the precise mechanism of the reaction is not yet clear. The dimeric molybdenum complex $[(cp)_2Mo_2(CO)_6]$ reacts with silver(I) trifluoroacetate to give the known[10] trifluoroacetato-derivative in low yield. However, the dimeric molybdenum complex is decomposed by either silver(I) nitrate or silver(I) hexafluoroantimonate.

Analytical and spectroscopic data

Complex	Found (%) C	Found (%) H	Found (%) N	Calc. (%) C	Calc. (%) H	Calc. (%) N	M.p. °C	ν(C≡O)[a] cm⁻¹	δ[b] p.p.m.
(IIb)	31·3	3·0		31·6	2·9		50	2075, 2030[c]	2·38(s) (co-ordinated acetone), 5·61(s) (C_5H_5)[d]
(VIII)	41·0	2·9	3·3	41·0	2·7	3·2	161 (decomp.)	2082, 2040	4·32(s) (CH_2), 5·60(s) (C_5H_5), 7·38(s) (C_6H_5)
(IX)	48·7	3·1	2·8	48·9	3·1	2·7	170 (decomp.)	2083, 2042	5·68(s) (C_5H_5), 5·95(s) (CH), 7·41(s) (C_6H_5)
(X)	37·6	3·1		37·6	2·9		145	2070, 2030	2·97(s), (CH_3), 5·66(s) (C_5H_5), 7·60(s) (C_6H_5)
(XVII)	56·0	3·4		56·4	3·4		97—98	2059, 2017[e]	5·27(s) (C_5H_5), 7·0—8·0(m) $C_6H_5)$
(XVIII)	48·6	3·8		48·3	3·4		94	2028, 2076	2·35(s) (CH_3), 5·30(s) (C_5H_5), 7·3(m) (C_6H_4)[f]
(XIX)								2010, 2062	*g*

[a] In $CHCl_3$ solution, except for complex (II) which was in CH_2Cl_2. [b] TMS internal standard. All spectra were measured in acetone-d_6 except for that of complex (II) in acetone. All spectra except that of complex (XVIII) (see footnote *f*) integrated correctly. s = Singlet, m = multiplet. Assignments in parentheses. [c] The carbonyl absorption of the co-ordinated acetone molecule occurs at *ca.* 1635 cm⁻¹. [d] Solvent acetone absorbs at 2·07 p.p.m. The resonances reported in ref. 3 for cation (II) appear to be in error. [e] The carbonyl group of the benzoate ligand absorbs at 1707 cm⁻¹. [f] Although analytically pure, complex (XVIII) must contain traces of paramagnetic impurity. Reasonably well resolved spectra were recorded only for freshly recrystallised samples and even here considerable broadening was evident. [g] Paramagnetic impurity evident, the spectrum was too broad for accurate determination of the resonance positions.

Despite the adverse price-factor involved in the use of silver-containing reagents, the synthetic routes described have much to recommend them. The oxidation is rapid and clean (removal of silver metal, the only by-product, by deposition from solution eliminates the necessity for tedious work-up procedures) and, in many cases, product yields are higher than those obtainable by other methods. This method should prove a useful supplement to the established synthetic procedures. Further extensions of the method are under study.

EXPERIMENTAL

Reagents and ligands were commercially available and were used as received without further purification. Reactions were carried out under an atmosphere of oxygen-free nitrogen, although this precaution could probably be dispensed with in most cases. N.m.r. spectra were measured at 60 MHz on a Perkin-Elmer–Hitachi R20A spectrometer and i.r. spectra were recorded using a Perkin-Elmer 257 spectrophotometer with grating optics. The essentials of the synthetic procedures are described below. Previously known complexes were identified by microanalysis and by comparison of i.r. and n.m.r. spectra with the published data. Spectroscopic and microanalytical data for the new complexes are collected in the Table.

Procedure.—(*A*). A solution of complex (I) and an excess of neutral ligand in oxygen-free acetone was treated with the appropriate silver(I) salt (ClO_4^-, PF_6^-, or SbF_6^-). When the i.r. spectrum of the reaction mixture indicated that the reaction had proceeded to completion, the reaction mixture was either reduced to a small volume and aqueous NH_4PF_6 added ($AgClO_4$), or evaporated to dryness ($AgPF_6$ and $AgSbF_6$) and the product recrystallised from acetone–ether or methylene chloride–ether. In the case of the iodo-complex (XIIb) alone, the ligand (as aqueous KI) was added ***after*** oxidation was complete. For the synthesis of the tricarbonyl cation (III), a solution of (I) in acetone was saturated with CO before addition of the oxidant and a stream of CO gas was maintained for 45 min after the addition. In this manner the following complexes were prepared (yields in parentheses): (IIb), 71; (III), 57; (IV), 85; (V), 60; (VII), 75; (VIII), 87; (IX), 62; (X), 74; (XI), 70; and (XIIb), 53%.

(*B*). Complex (I) and the appropriate silver(I) salt were stirred at room temperature in acetone solution until i.r. measurements indicated that reaction was complete. The time required varies from *ca.* 30 min for the nitrato-complex (XIII) to *ca.* 2 days for the benzoato-complex (XVII). After filtration the solution was concentrated to dryness and the residue recrystallised from methylene chloride–hexane. In one case, the thiocyanato-complex (XV), heating under reflux for 24 h was necessary to induce reaction. Rather surprisingly, the *N*-bonded isomer was not isolated under these conditions. In this manner the following complexes were prepared (yields in parentheses): (XIII), 60; (XIV), 87; (XV), 50; (XVI), 70; (XVII), 42; and (XVIII), 75%. The diphenyl phosphato-complex (XIX) prepared in this fashion was unstable, could not be purified, and was identified on the basis of its i.r. spectrum.

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[8] F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc.* (*C*), 1969, 2719.

[9] D. Cashman and F. J. Lalor, *J. Organometallic Chem.*, 1971, **32**, 351.

[10] R. B. King and R. N. Kapoor, *J. Organometallic Chem.*, 1968, **15**, 457.

A similar procedure was used to prepare the complex [(cp)Mo(CO)$_3$O$_2$CCF$_3$] (in *ca.* 40% yield) from [(cp)$_2$Mo$_2$(CO)$_6$] and AgO$_2$CCF$_3$.

(*C*). *Preparation of the Complex* [(cp)Fe(CO)$_2$(SbPh$_3$)]$^+$PF$_6^-$ (VI). Complex (IIb) (0·5 g, 1·3 mmol) was dissolved in oxygen-free CH$_2$Cl$_2$ (40 ml). Ph$_3$Sb (1·0 g, *ca.* 2·8 mmol) was then added and the solution stirred overnight. After filtration through Celite the solution was concentrated and diluted with ether, giving yellow crystals of the complex [(cp)Fe(CO)$_2$SbPh$_3$]$^+$PF$_6^-$ in 40% yield.

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