Redox-catalysed Isomerisation of Manganese Carbonyl Derivatives

Neil G. Connelly,[a] Stephen J. Raven,[a] Gabino A. Carriedo,[b] and Victor Riera[b]

[a] *Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS, U.K.*
[b] *Department of Inorganic Chemistry, University of Oviedo, Spain*

The isomerisation of the manganese(I) complex *trans*-[MnBr(CO)$_2${P(OPh)$_3$}(dppm)] [dppm = bis(diphenylphosphino)methane, Ph$_2$PCH$_2$PPh$_2$] to *cis,cis*-[MnBr(CO)$_2${P(OPh)$_3$}(dppm)] is catalysed by the manganese(II) cation *trans*-[MnBr(CO)$_2${P(OPh)$_3$}(dppm)]$^+$.

The oxidatively-induced isomerisation of chromium and manganese group carbonyl derivatives is well-documented,[1] with the reaction sequence described by a 'square-scheme' as generalised below for two geometric isomers, A and B. Bond and co-workers[2] have studied extensively the electrochemistry associated with such schemes and have noted that certain cyclic voltammetric parameters (particularly wave shapes) are only fully explicable if the cross redox reaction A$^+$ + B $\rightleftharpoons$ A + B$^+$ is also taken into account. We now show that this cross reaction has an important synthetic consequence in leading to the catalytic isomerisation of metal carbonyl derivatives.

The oxidative behaviour of *cis,cis*-[MnX(CO)$_2${P(OPh)$_3$}-(dppm)]^Z [(1); $Z = 0$, X = Br, CN, or NCS; $Z = +1$, X = NCMe, CNMe, *etc.*; dppm = Ph$_2$PCH$_2$PPh$_2$] is similar to that[3] of *fac*-[MBr(CO)$_3$(L–L)] (M = Mn or Re, L–L = dppm *etc.*); the cyclic voltammogram of (1) shows one irreversible one-electron oxidation wave (*e.g.* X = Br, $E_{pk} = 0.89$ V at a scan rate of 200 mV s^{-1}) and a reversible product wave at a
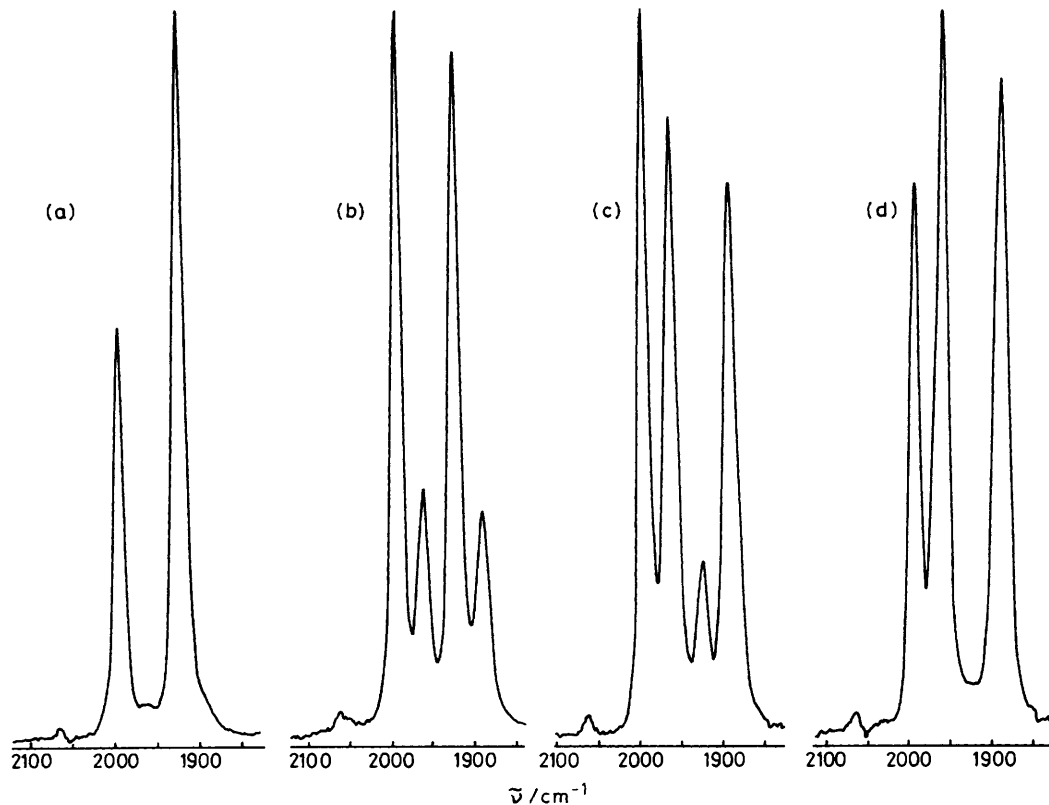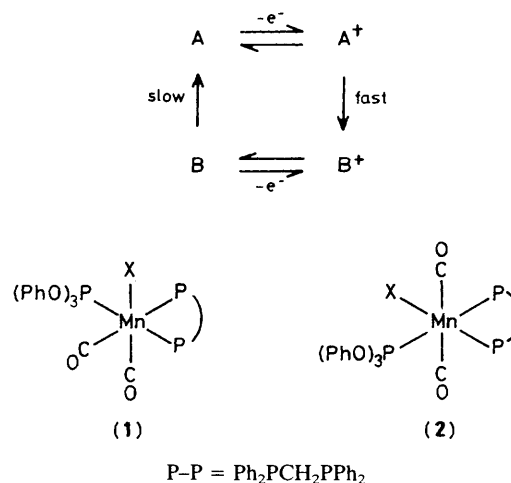

P–P = Ph$_2$PCH$_2$PPh$_2$

Figure 1. The i.r. spectrum (a) of a mixture of (**2**, X = Br) and (**2$^+$**, X = Br) (4:1, CH$_2$Cl$_2$), (b) after 70 min, (c) after 180 min, (d) after 220 min.
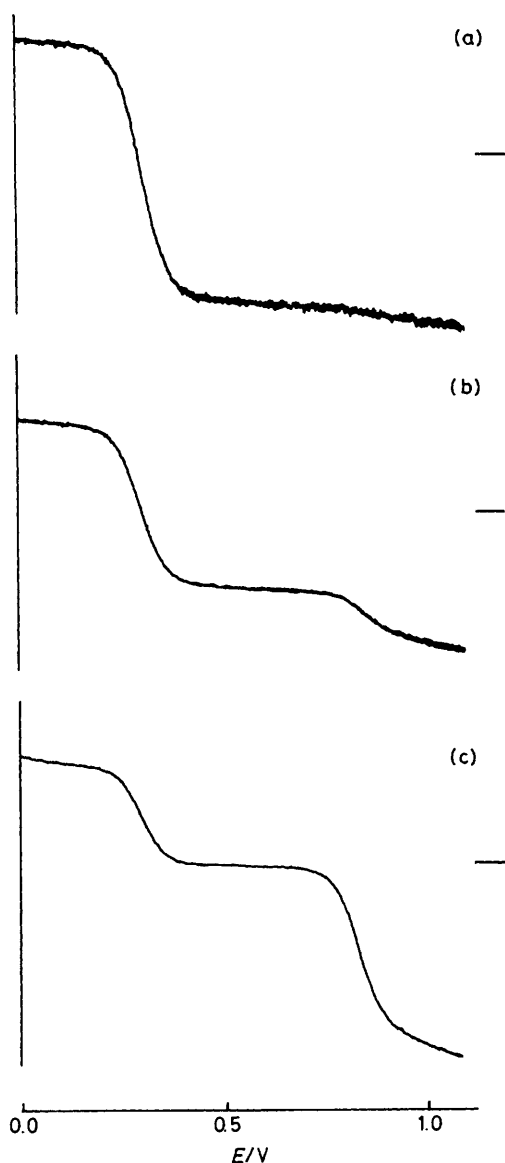
Figure 2. The rotating platinum electrode voltammogram (a) of (2, X = Br) after partial electrolysis (n = 0.38) at 0.55 V [the ratio of (2, X = Br) to (2$^+$, X = Br) is 3:2], (b) after 120 min, (c) after 345 min. The horizontal line represents zero current.

more negative potential (*e.g.* X = Br, E^0 = 0.31 V).† Chemical {[NO][PF$_6$]} or electrochemical (*e.g.* X = Br, $E_{applied}$ = 1.0 V) oxidation of (1, X = Br) in CH$_2$Cl$_2$ quantitatively gave *trans*-[MnX(CO)$_2${P(OPh)$_3$}(dppm)]$^+$ (2$^+$), [*e.g.* X = Br, deep red, $\tilde{v}$(CO) 1994 cm^{-1}] which showed one reversible, one-electron reduction wave (E° = 0.31 V).

These results are described by the 'square scheme'; oxidation of (1) to (1$^+$) is followed by rapid isomerisation to (2$^+$). Thus, in agreement with this scheme, reduction of (2$^+$,

X = Br) in CH$_2$Cl$_2$ with an excess of [NBu$^n_4$][BH$_4$] or by exhaustive electrolysis at 0.0 V gave a quantitative yield of (2, X = Br), [red, $\tilde{v}$(CO) 1923 cm^{-1}] which does not isomerise to (1, X = Br) at room temperature in 12 h. Remarkably, however, partial reduction of (2$^+$), for example using a deficiency of [NBu$^n_4$][BH$_4$], or partial oxidation of (2), for example *via* electrolysis (n < 1), leads to the catalysed formation of (1) in quantitative yield.‡

Figure 1 shows the variation with time of the i.r. spectrum of a mixture, initially of (2, X = Br) and (2$^+$, X = Br) in a 4:1 ratio; as (1, X = Br), [$\tilde{v}$(CO) 1961 and 1889 cm^{-1}] forms at the expense of (2) the concentration of (2$^+$) remains constant.

The isomerisation was also monitored by voltammetry at a rotating platinum electrode. Figure 2(a) shows the voltammogram after partial electrolytic oxidation ($E_{applied}$ = 0.55 V, n = 0.38) of (2) to (2$^+$); the wave at 0.3 V has oxidative and reductive components (2:3 ratio). As (2) is converted into (1), Figures 2(b,c), the wave at 0.3 V is reduced in height (but the oxidative component remains constant) while the wave at 0.89 V, due to (1), is increased. After 6 h only (2$^+$) and (1) are present in solution, in a 2:3 ratio.

These results, described for the bromide complex but general for X = CN, CNMe *etc.*, can only be interpreted in terms of a catalytic cycle in which the cross redox reaction (1$^+$) +(2) ⇌ (1) + (2$^+$) is linked to the isomerisation reaction (2$^+$) ⇌ (1$^+$). Although the latter equilibrium lies far to the left, the cross redox reaction, for which $K \approx 2 \times 10^9$ [estimated from the difference between the potentials for the oxidations of (1) and (2)], provides the driving force for the catalytic cycle.

These observations are important for two reasons. First, such catalytic processes may profoundly influence the isomer distribution observed during and after electron-transfer reactions of metal carbonyls in their ground states. Second, these processes must be considered in the excited state; there is current interest in photoelectron-transfer reactions of species such as *fac*-[ReX(CO)$_3$(L–L)]^Z, for example in CO$_2$ reduction (Z = 0, X = Cl or Br, L–L = bipyridyl)[4] and photosubstitution (Z = 1, X = NCMe, L–L = *o*-phenanthroline).[5]

References

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† All electrochemical measurements were carried out in CH$_2$Cl$_2$, 0.1 mol dm^{-3} in [NBu$^n_4$][PF$_6$] as supporting electrolyte. Voltammetry employed a platinum bead electrode, controlled potential electrolysis a platinum basket. All potentials are quoted *vs.* the saturated calomel electrode; E^0 for the oxidation of ferrocene, added as an internal standard, is 0.47 V under the experimental conditions used.

‡ The isomerisation process is immediately halted if (2$^+$, X = Br) is removed from the reaction mixture by quenching with an excess of [NBu$^n_4$][BH$_4$].