Electron Transfer in Oxidative Addition Reactions of d^6-Metal Complexes

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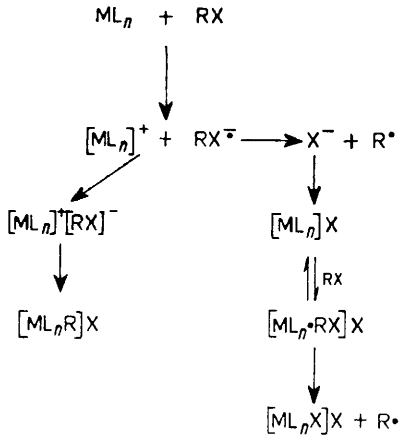
Summary In the reaction of *cis*-$[Mo(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ with alkyl halides, electron transfer from the metal substrate to the addendum involves the oxidation of Mo^0 to Mo^{II} with Mo^I as the identified paramagnetic intermediate.

The mechanism of the oxidative addition process in which, for example, an organic halide RX, reacts with a transition-metal compound, ML_n, to form $[ML_n(R)(X)]$ has been studied extensively.[1] More recently, it has become clear that free-radical intermediates may be involved[2], although the identity of the metal-centred species is not well defined. All previous mechanistic work has concerned additions to metal complexes in which the metal has either a d^8 or a d^{10} electron configuration.

We have reported that the compound *cis*-$[Mo(CO)_2(dmpe)_2]$, (**1**), (dmpe = $Me_2PCH_2CH_2PMe_2$) reacts with various molecules RX to form *cis*-$[MoX(CO)_2(dmpe)_2]X$, (**2**), and R–R.[3] We have extended these investigations and obtained information about the mechanism of these reactions. When the reaction between (**1**) and Ph_3CCl in acetonitrile is carried out in the cavity of an e.s.r. spectrometer, signals are observed which can be assigned unambiguously to *trans*-$[Mo(CO)_2(dmpe)_2]^+$ and to the $Ph_3C\cdot$ radical. The identity of the Mo^I species was confirmed by measurements on pure *trans*-$[Mo(CO)_2(dmpe)_2]BF_4$ [ν(CO) 1858 cm^{-1} (MeCN); $g = 2{\cdot}053$, $a = 25$ G; λ_{max} 447 nm]. This is the first report of the positive identification of both the metal-centred paramagnetic intermediate and the organic free radical in reactions of this kind. The final products of the reaction were (**2**; X = Cl) and Ph_6C_2.

Examination of the reactions between (**1**) and other alkyl halides ($PhCH_2Br$, CCl_4) in acetonitrile solution showed that the same Mo^I intermediate was formed in each case, and the rate of its production and subsequent conversion into (**2**) was monitored by i.r., visible, and e.s.r. spectrometry. The picture which emerges from studies of the concentration dependence of the rate of the reaction with both CCl_4 and $PhCH_2Br$ is of an initial, rate-determining, bimolecular reaction in which an electron is transferred from (**1**) to form *cis*-$[Mo(CO)_2(dmpe)_2]^+$, (**3**), and $RX^{\cdot-}$ [rate at 293 K (for CCl_4) *ca.* 2×10^{-2} mol l^{-1} s^{-1}], followed by isomerisation of (**3**) to produce *trans*-$[Mo(CO)_2(dmpe)_2]X$, (**4**), and R·. The production of (**3**) from (**1**) is much more rapid (rate at 293 K *ca.* 10^4 mol l^{-1} s^{-1}) when Ph_3CCl is used. An equilibrium is then rapidly established between (**4**) and a second molecule of RX to form an adduct, [(**4**)·RX] which decomposes in a first-order reaction [rate at 293 K *ca.* 3×10^{-3} s^{-1} (CCl_4, $PhCH_2Br$), 2 s^{-1} (Ph_3CCl)] to form (**2**) and R–R. We are unable to detect whether the outer sphere halide ion in (**4**) is identical with that in (**2**) but suggest that this is likely.



Scheme

The reaction between (**1**) and $C_2(CN)_4$ (TCNE) in acetonitrile at room temperature proceeds *via* the TCNE radical anion (e.s.r., u.v.–visible spectra) to give only the σ-tricyanovinyl[4] complex *cis*-$[Mo\{C_2(CN)_3\}(CO)_2(dmpe)_2]CN$, (**5**) [ν(CO) 1950vs, 1900s; ν(CN) 2210w, 2170m, 2160m; ν(CN^-) 2082vs; ν(C=C) 1435m cm^{-1} (KBr)] which is formally similar to the product of the reaction between $[Pt(PPh_3)_2(stilbene)]$ and *trans*-$[CF_3(CN)C]_2$ which is[5] *trans*-$[Pt(PPh_3)_2(CN)\{C(CF_3):C(CF_3)(CN)\}]$. The formation of both the Mo^I cation and the corresponding organic anion radical is observed when (**1**) is mixed with 1,3,5-trinitrobenzene and with 1,2,4,5-tetracyanobenzene in acetonitrile solution. The identity of the Mo^{II} products which have been isolated from these reactions will be described separately.

These results indicate the following conclusions which may be applicable in other systems. First, the oxidative addition reaction is initiated by an electron transfer from the readily ionizable[†] (oxidizable) metal substrate to the addendum, RX, which is to be regarded as an electron acceptor (*cf.* gas-phase electron affinity, CCl_4 2·12,[6] TCNE 2·89 eV[7]), so as to produce the anion radical, $RX^{\cdot-}$. Secondly, $RX^{\cdot-}$ may decompose (*e.g.* CCl_4[8]) to give R· radicals and X^- ions which then serve to stabilise the oxidized paramagnetic metal system [*e.g.* (**4**; X = Cl) in the case of CCl_4 and Ph_3CCl]. Thirdly, nucleophilic attack, by RX on the oxidized metal system [*e.g.* (**4**)], or within the radical pair {*e.g.* $[Mo(CO)_2(dmpe)_2]^+[TCNE]^-$}, will lead to the product (**2**) or its analogue (**5**). These points are summarized in the Scheme.

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[†] *Added in Proof*: $[Mo(CO)_2(dmpe)_2]$, first I.P. = 6·00 (vertical) and 5.47 (adiabatic) eV (D. R. Lloyd, Birmingham University, personal communication); $E^{ox}_{\frac{1}{2}} = -0{\cdot}23$ V in CH_2Cl_2 (M. K. Lloyd, J. A. McCleverty, D. G. Orchard, J. A. Connor, M. B. Hall, I. H. Hillier, E. M. Jones, and G. K. McEwen, *J. C. S. Dalton*, 1973, 1743).

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