

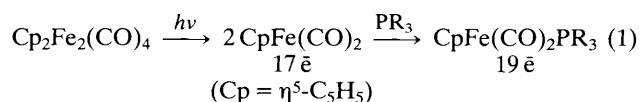
## Reduction of Water-soluble Substrates in Micellar Solutions using photochemically generated Nineteen-electron Organometallic Complexes

Vivian MacKenzie and David R. Tyler\*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403, U.S.A.

Nineteen-electron organometallic complexes were generated photochemically in the benzene phase of micellar and reverse micellar solutions; methylviologen and ferricyanide were reduced in order to demonstrate that these powerful reducing agents can be used to reduce water-soluble substrates contained in the aqueous phase.

Several years ago we reported that photochemically-generated 17-valence electron metal radicals react with ligands to form 19-electron complexes,<sup>1,2</sup> *e.g.* reaction (1).<sup>1</sup> The 19-electron complexes are versatile reducing agents and we reported that they can be used to reduce a variety of organic, organometallic, and inorganic complexes,<sup>2,3</sup> *e.g.* reaction (2). In addition to their versatility, two other features make the 19-electron complexes ideal choices as reducing agents for many applications. First, the complexes are easy to generate; the metal-metal bonded dimers are convenient precursors and the wavelength of irradiation ( $\lambda > 500$  nm) generally precludes substrate absorption. Second, the 19-electron complexes are very powerful reducing agents. In some cases we estimate their oxidation potential to be 2 V or higher.<sup>2</sup>



S = CpMo(CO)<sub>3</sub>Cl, methylviologen (1,1'-dimethyl-4,4'-bipyridinium dication; MV<sup>2+</sup>), Cp<sub>2</sub>Co<sup>+</sup>, Ru<sub>3</sub>(CO)<sub>12</sub>, *N*-*n*-butylpyridinium, Mn<sub>2</sub>(CO)<sub>10</sub>

Despite these attractive features, one drawback in the application of the 19-electron complexes is that because they are generated from organometallic precursors, they must be used in non-aqueous solvents. Thus, substrates that are soluble only in water cannot be reduced by the 19-electron complexes. This drawback limits the application of these

reductants, particularly in problems of biological interest and in solar energy conversion schemes. To surmount this problem, we studied the generation and reactivity of the 19-electron complexes in aqueous micellar solutions. In this communication, we report the successful reduction of water-soluble substrates using micellar solutions to solubilize the organometallic precursors in aqueous solutions.

The key to the successful reduction of the substrates is the proper preparation of the micellar solutions. In a typical preparation Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> (5 mg) was dissolved in benzene (0.25 ml). This solution (20  $\mu$ l) was then added to 3 ml of an aqueous solution containing the substrate to be reduced (typically about 10<sup>-3</sup> M) and the surfactant CTAB (1.6  $\times$  10<sup>-3</sup> M; CTAB = hexadecyltrimethylammonium bromide). PBu<sub>3</sub> (5  $\mu$ l) was then added to the solution. (PBu<sub>3</sub> could also be added to the benzene solution before mixing with the aqueous solution. In either case, an excess of PBu<sub>3</sub> must be avoided to prevent clouding the combined solutions.) The combined solutions, consisting of two phases, were then stirred or shaken for *ca.* 1 min., after which time the solution was homogeneous. The solution was then transferred to the appropriate spectroscopic cell or cuvette and irradiated ( $\lambda > 500$  nm). When the substrate was MV<sup>2+</sup>, *e.s.r.* and electronic absorption spectra of the reaction solution after irradiation clearly showed the formation of MV<sup>+</sup>; the spectra were identical to those previously reported for MV<sup>+</sup>.<sup>4,5</sup> The choice of phosphine ligand used to generate the 19-electron complex is not critical. Thus, for example, 1,2-bis(diphenylphosphino)ethane (dppe) gave results identical to those obtained above with PBu<sub>3</sub>.

It is logical to propose that a 19-electron CpFe(CO)<sub>2</sub>PBu<sub>3</sub> complex is the reducing agent in the reaction above. Unfortunately, *i.e.* detection of the CpFe(CO)<sub>2</sub>PBu<sub>3</sub><sup>+</sup> cation was

impossible in the micellar solution. However, i.r. analysis of reactions run in MeCN<sup>†</sup> showed the formation of CpFe(CO)<sub>2</sub>PBu<sub>3</sub><sup>+</sup> [ $\nu(\text{C}\equiv\text{O})$  2049 and 2003 cm<sup>-1</sup>]. In addition, electronic absorption spectroscopic analysis of reactions run in MeCN also showed that *ca.* 2 moles of MV<sup>+</sup> were formed for every mole of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> consumed, consistent with the stoichiometry in equations (1) and (2).

In addition to regular micelles, MV<sup>2+</sup> can also be reduced in reverse micellar solutions. The procedure is essentially identical to that above except that didodecyldimethylammonium bromide (DDAB) is used as the surfactant and the amounts of benzene and aqueous solution are reversed. MV<sup>+</sup> was again detected by electronic absorption and e.s.r. spectroscopy.

Other complexes which are soluble in water but insoluble in organic solvents can also be reduced in micellar solutions, *e.g.* K<sub>3</sub>Fe(CN)<sub>6</sub>. This complex was reduced by a procedure essentially identical to the one described above for MV<sup>2+</sup>, the

only difference being that sodium dodecyl sulphate was used as the surfactant. The product of the reduction was Prussian Blue ( $\lambda_{\text{max}}$  718 nm in the reaction solution).

The mechanism of the reductions reactions is being investigated.

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<sup>†</sup> [MV<sup>2+</sup>]Cl<sub>2</sub> was first dissolved in a small amount of water and this solution was added to MeCN.