Correspondence

A Reply to the Reports of Ginsberg et al. and Eisenberg et al. on the Electrochemical Reduction of $[Ir(DPE)_2]^+$ and $[Rh(DPE)_2]^+$ (DPE = 1,2-Bis(diphenylphosphino)ethane)

Sir:

Ginsberg et al.[1] and Eisenberg et al.[2] have reported that the electrochemical reduction of $[M(DPE)_2]^+$ (M = Rh, Ir) proceeds by an ECE mechanism.[3] These results contrast with our previous report,[4] which concluded that in the electrochemical reduction of these complexes an EC mechanism is involved.[5] It was, of course, essential that this discrepancy between our report and theirs was resolved. Therefore we have thoroughly reexamined the electrochemical behavior of the title compounds and the results are here presented.

The polarographic pattern of $[Rh(DPE)_2](ClO_4)$ in acetonitrile containing 0.1 M Et_4NClO_4 as supporting electrolyte is consistent within the range of drop time 1.0–10 s with a single, diffusion-controlled, two-electron reversible transfer, i.e.: (i) the logarithmic analysis of the wave resulting in a straight line with slope equal to 30 mV; (ii) $E_{1/2}$ (−2.10 V vs. Ag/0.1 M Ag^+ acetonitrile electrode) independent of drop time; (iii) I_d[6] = 4.4. As a confirmation, the isoelectronic and isostructural cobalt complex $[Co(DPE)_2](ClO_4)$, under identical experimental conditions, shows two one-electron, diffusion-controlled, reversible waves with $I_d = 2.2$ for each step.[7,8] On the contrary, for an overall two-electron ECE reduction with an irreversible chemical step and the product couple more readily reduced than the parent couple,[2] the slope of the conventional log plot for the polarographic wave should correspond to the transfer of a single electron, i.e., 59 mV. Only the current magnitude is a function of the number of electrons transferred, and it increases when the chemical reaction is kinetically significant in the time scale of experiments, as the drop time increases.[9]

Cyclic voltammetric experiments with achievement of ohmic drop compensation by a positive feedback network on a planar gold microelectrode freshly coated with mercury (approximate area 0.3 mm^2) show the following in the range of scan rate, V, from 20 to 1000 mV s^{-1}: (i) $i_pV^{-1/2}$ independent of V; (ii) i_p about 2.8 times that for each of the two one-electron transfers of $[Co(DPE)_2]^+$; (iii) i_p^a/i_p^c equal to unity and independent of V; (iv) $E_p^c - E_p^a$ and $E_p - E_{p/2}$ equal to 30 ± 2 mV, with full agreement with the polarographic data. In contrast with these observations, for a two-electron reaction with an irreversible chemical step and the second transfer anodic to the first,[2] the current should be at most 2.2 times that of a reversible one-electron process,[10] and $E_p - E_{p/2}$ should be equal to 48 mV in the limiting case of a purely kinetically controlled two-electron transfer, while at the other extreme being 57 mV for a purely diffusion-controlled one-electron exchange.[11] Also, Magno[12] has recently found, using a digital simulation technique, that the expected variance in peak potential separation, $E_p^c - E_p^a$, with scan rate for an ECE mechanism of this type is exactly in the opposite direction to that which the title authors have claimed in support of such a reduction mechanism; i.e., concomitant with the increase in the ratio of reduction peak current to the oxidation peak current, i_p^c/i_p^a, an increase in $E_p^c - E_p^a$ above 59 mV is observed.[13]

As far as the iridium complex $[Ir(DPE)_2](ClO_4)$ is concerned, it gives polarographic (height and log plot slope of the wave) and cyclic voltammetric (reduction peak current and peak potential separation) responses virtually identical with those found for the rhodium analogue under similar conditions (see above). The one exception is that the anodic to cathodic current ratio, i_p^a/i_p^c, is less than unity and increases as V increases with unity approached at values of $V \geq 1$ V s^{-1}.

Consequently all our data point unequivocally for both complexes to a two-electron, essentially reversible charge-transfer process, followed for the iridium derivative by a chemical reaction[5] already recordable in the time window of the experiment. The different conclusions drawn by the aforementioned authors could arise from their evaluation of the number of exchanged electrons based mainly on the variance in peak potential separation with scan rate, even though current measurements possess better properties.[11,14] In addition to the above defect, their approach is not very reliable because direct compensation of ohmic contribution to peak separation is lacking.[2]

The d^{10} species $[M(DPE)_2]^-$ being really the primary reduction product has been confirmed for the rhodium derivative by potentiostatic reduction of $[Rh(DPE)_2]^+$ in carefully dried[15] acetonitrile at low temperature (−35 °C), which prevents the reduction product from being immediately quenched by the solvent. In fact, at the end of the electrolysis (requiring 2 equiv of electrons/mol of depolarizer) the spent ruby red catholyte shows a reversibly shaped anodic wave at the same potential ($E_{1/2} = -2.10$ V) and about 20% lower than that of the starting compound. With time ($t_{1/2} \simeq 1000$ s at −35 °C) this wave disappears while the hydride, $HRh(DPE)_2$, precipitates. The recovery of $DRh(DPE)_2$, when such an electrolysis is performed in CD_3CN, indicates that the main source of hydrogen is acetonitrile and suggests that the interaction between the d^{10} anionic species and the solvent may be easily accommodated on the basis of a generalized acid–base equilibrium.[16]

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(1) B. K. Teo, A. P. Ginsberg, and K. C. Calabrese, *J. Am. Chem. Soc.*, **98**, 3027 (1976).
(2) J. A. Sofranko, R. Eisenberg, and J. A. Kampmeier, *J. Am. Chem. Soc.*, **101**, 1042 (1979).
(3) The electrochemical reduction is claimed to proceed via a one-electron transfer, generating the zerovalent compound followed by H atom abstraction from the solvent to give the metal hydride and subsequent reduction of the solvent radical.
(4) G. Pilloni, E. Vecchi, and M. Martelli, *J. Electroanal. Chem. Interfacial Electrochem.*, **45**, 483 (1973).
(5) A single two-electron reduction to yield an anionic intermediate quenched by proton abstraction from the medium to give the metal hydride.
(6) $I_d = i_dC^{-1}m^{-2/3}t^{-1/6}$, where i_d is expressed in μA, C in mmol L^{-1}, m in mg s^{-1}, and t in s.
(7) G. Pilloni, G. Zotti, and M. Martelli, *J. Electroanal. Chem. Interfacial Electrochem.*, **50**, 295 (1974).
(8) The one-electron reduction product is the well-known $Co(DPE)_2$: C. F. Nobile, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **5**, 698 (1971).
(9) H. Matsuda, *J. Electroanal. Chem. Interfacial Electrochem.*, **56**, 165 (1974).
(10) R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 190 (1965).
(11) M. Mastragostino, L. Nadjo, and J. M. Saveant, *Electrochim. Acta*, **13**, 721 (1968).
(12) F. Magno, submitted for publication in *Anal. Chem.*
(13) Erroneously quoting Nicholson and Shain,[14] Eisenberg et al. infer that the expected behavior for an ECE reduction of this type is a decrease in $E_p^c - E_p^a$. Those authors really did not discuss the ECE mechanism on the grounds of dependence of peak potential separation on scan rate; on the contrary, current functions were extensively considered.
(14) R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 178 (1965).
(15) C. K. Mann, "Electroanalytical Chemistry", Vol. 3, Marcel Dekker, New York, 1969, p 69.

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Table I. Typical Determination of the Rate Constant for the Chemical Step in the Reduction of $[Rh(DPE)_2]^+$ (2.0×10^{-4} M) in Wet (0.07 M H_2O) Acetonitrile (0.1 M Et_4NClO_4) Solution at 25.0 °C

scan rate, V s^{-1}	i_p^a/i_p^c	$k_{obsd}\tau$	τ, s	k_{obsd}, s^{-1}
0.020	0.45	1.30	11.0	0.12
0.050	0.63	0.55	4.40	0.13
0.100	0.77	0.28	2.20	0.13
0.200	0.87	0.14	1.10	0.13

Table II. Dependence on the Concentration of Water of the Rate Constants for the Chemical Step in the Reduction of $[M(DPE)_2]^+$ in CH_3CN (0.1 M Et_4NClO_4) Solution at 25.0 °C

M = Rh		M = Ir	
$[H_2O]$, mM	k_{obsd}, s^{-1}	$[H_2O]$, mM	k_{obsd}, s^{-1}
26	0.014	10	1.0
48	0.050	17	2.2
70	0.13	26	4.0
93	0.24	40	8.7
115	0.44	48	13
137	0.78		
160	1.3		

As a matter of fact, CH_3CN is currently reported to act as a proton donor toward some classes of electrochemically generated organic anions.[18] Furthermore, the freshly reduced red solution (see above), upon addition of excess carbon monoxide, quickly turns yellow while 1 mol of DPE precipitates. The infrared spectrum of the solution (bands at 1805 and 1860 cm^{-1}) shows that $[Rh(CO)_2(DPE)]^-$ has formed.[19] Also, the addition of $ClSnPh_3$ to the carbonylated solution allows the d^{10} anion to be isolated.[19] It is noteworthy that the polarogram of the spent yellow catholyte does not exhibit any cathodic wave, thus ruling out the disproportionation by CO of a hypothetical d^9 derivative.[20,22]

In our previous paper[4] we reported and hereby confirm that deliberate addition of increasing amounts of water leads to the stepwise disappearance of the coupled anodic peak, *the cathodic peak being unchanged*, in the cyclic voltammograms of both $[Rh(DPE)_2]^+$ and $[Ir(DPE)_2]^+$. Interestingly, at any selected concentration of water the ratio of peak currents, i_p^a/i_p^c, as a function of the time, τ, required to scan from $E_{1/2}$ to the switching potential, E_λ, fits the Nicholson–Shain working curve for an EC process,[24] thus providing additional evidence for the considered mechanism and allowing the rate constant values for the chemical step to be calculated. This is exemplified in Table I. So far as the dependence of the observed rate constants on the concentration of added water (Table II), the change in order for water at increasing concentrations may be easily rationalized by the presence of more acidic water polymers. D_2O causes the same effect even though no $DRh(DPE)_2$ or $DIr(DPE)_2$ is recovered in preparative electrolyses under these conditions.[1,2] Identical chemical behavior is, however, shown by the one-electron reduction product of $Co(DPE)_2$, viz., $[Co(DPE)_2]^-$, which appears to be quenched mainly by proton abstraction from acetonitrile, as $HCo(DPE)_2$ is formed in CH_3CN with small amounts of D_2O while $DCo(DPE)_2$ is obtained in CD_3CN in the presence of low concentrations of H_2O.

The inconsistency of the D-labeling results could still be solved with the assumption of the likely occurrence of a rapid H/D exchange reaction converting D_2O into H_2O or H_2O into D_2O in CH_3CN or CD_3CN, respectively. As a matter of fact we have found that such an exchange reaction does indeed occur quickly and, for low concentrations of water, quantitatively on the condition that OH^- or OD^-, even in trace amounts, is present.[25]

In line with the EC mechanism, hydroxide ions are produced in the hydride formation already in the early stages of the electrolyses in wet solvents in view of the highly protic nature of water relative to acetonitrile. As a consequence, no sooner do such electrolyses start than the H/D exchange also begins and goes to completion in a very short time.[26]

In conclusion, the labeling experiments that, according to the title authors, should have provided the strongest evidence of the radical nature of the primary reduction product thus lose any meaning.

Registry No. $[Rh(DPE)_2]^+$, 47895-57-8; $[Ir(DPE)_2]^+$, 29871-99-6.

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(16) In a subsequent paper, which appeared while this reply was submitted for publication, Eisenberg et al.[17] report that in benzonitrile the primary source of hydrogen for rhodium hydride formation is the electrolyte, tetrabutylammonium perchlorate, and not the solvent, since 1-butene and tributylamine are formed. The authors themselves, while claiming once more the ECE character of the overall process, acknowledge that "the formation of Hofmann degradation products from the reaction of electrochemically generated anionic intermediates with tetraalkylammonium salts is not uncommon".

(17) J. A. Sofranko, R. Eisenberg, and J. A. Kampmeier, *J. Am. Chem. Soc.*, **102**, 1163 (1980).

(18) See, for example A. J. Bellamy, *J. Chem. Soc., Chem. Commun.*, 944 (1975); K. P. Butin, M. T. Ismail, and O. A. Reutov, *J. Organomet. Chem.*, **175**, 157 (1979).

(19) G. Pilloni, G. Zotti, and M. Martelli, *Inorg. Chim. Acta*, **13**, 213 (1975).

(20) All the chemical reactions reported for $Rh(DPE)_2$ may be easily be accommodated on the basis of $[Rh(DPE)_2]^-$ formation. In particular, the quoted[2] radical products formation could be accounted for by an oxidative addition reaction of the organic halide to the d^{10} complex, $[Rh(DPE)_2]^-$, followed by dissociative reduction of the resulting organometallic derivative. Related behavior has already been found, for instance, in $[Ni(CH_3)(P(CH_3)_3)_4]^+$, which undergoes reductive elimination to give $[Ni(P(CH_3)_3)_4]^+$.[21]

(21) A. Gleizes, M. Dartinguenave, Y. Dartinguenave, and H. F. Klein, *J. Am. Chem. Soc.*, **99**, 5187 (1977).

(22) As far as the alleged d^9 species is concerned, Mulazzani et al. have produced it by pulse radiolysis in methanol.[23] This transient species has a half-life that appears beyond the reach of cyclic voltammetry, and its fate is oxidation by the solvent back to $[Rh(DPE)_2]^+$ without formation of a metal–hydrogen bond.

(23) Q. G. Mu'azzani, P. G. Fuochi, G. Pilloni, and E. Vecchi, *Int. J. Radiat. Phys. Chem.*, **10**, 275 (1977).

(24) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(25) The conversion of D_2O and vice versa in acetonitrile has been evidenced by IR measurements in 0.05-cm CaF_2 liquid cells with compensation of the bands of D_2O (2700, 2600, and 1200 cm^{-1}) and H_2O (3640, 3540, and 1630 cm^{-1}) of the solutions (1 mol % or less of water) before and after addition of tetraethylammonium hydroxide ($\geq 2 \times 10^{-5}$ M).

(26) A typical electrolysis performed on a 2×10^{-3} M solution of $[Rh(DPE)_2]^+$ in CH_3CN in the presence of D_2O (≈ 1 mol %) has shown that full conversion of D_2O into H_2O has already taken place after 1% of the exhaustive amount of charge had been allowed to pass.

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Proton Relaxation Enhancement in Paramagnetic Dinuclear Transition-Metal Complexes

Sir:

The magnetic interactions in dinuclear metal complexes have been intensively investigated, mainly through magnetic susceptibility measurements and EPR spectroscopy.[1-10] Far less

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(1) Kokoszka, G. F.; Duerst, R. W. *Coord. Chem. Rev.* **1970**, *5*, 209.