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REDOX BEHAVIOUR OF GROUP VIIB METAL—METAL BONDED CARBONYLS: SUBSTITUTION EFFECTS

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Summary

Electrochemical reduction parameters of $M_2(CO)_{10}$ (M_2 = Mn_2, MnRe, Re_2) (I) are compared with those of the related axially disubstituted $M_2(CO)_8(PPh_3)_2$ (II) compounds. With compounds II, the half-wave potentials are more cathodic than with compounds I. The same results are obtained from cyclic voltammetry on platinum electrode. From the electronic absorption spectra of compounds I and II, the energies of the $\sigma \rightarrow \sigma^*$ transitions associated with the metal—metal bond are calculated. In $Mn_2(CO)_{10}$ and $MnRe(CO)_{10}$ these energies correlate well with the electrochemical results: replacement of two axial CO groups by PPh_3 weakens the metal—metal bond. In contrast for $Re_2(CO)_{10}$ the same substitution reinforces the rhenium—rhenium bond.

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1. Introduction

Earlier studies [1] of the electrochemical reduction of $M_2(CO)_{10}$ (M = Mn, Re) indicate that the slow electrochemical reduction step leads to the reactive anionic intermediate $[M(CO)_5]^-$. Mechanistic information has also been obtained for similar electroreduction of $MnRe(CO)_{10}$ [2] molecule, leading to $[Mn(CO)_5]^-$ and $[Re(CO)_5]^-$. The electrochemical reduction of symmetrical Group VIIB metal—metal bonded carbonyls thus results in metal—metal bond cleavage. For electrochemically reversible systems, a simple relationship could relate the half-wave reduction potentials to the metal—metal bond energy, but as the systems studied here are slow there is no direct quantitative correlation between the reduction potentials and the metal—metal bond strengths. In the present work we intended to measure the electrochemical reduction rate constants for axially disubstituted $M_2(CO)_8(PPh_3)_2$ (M_2 = Mn_2, MnRe, Re_2) and compare them with those for related $M_2(CO)_{10}$ molecules. We also examined the consequence of substitution of CO by PPh_3 on the cleavage of the metal—metal bond. They are few quantitative studies related to the strengths of the metal—metal bond in such compounds [3], and the results obtained by spectroscopic [3—10], mass spectrometric [11,12] or theoretical studies [13] are not all consistent. Previously all studies indicated that the metal—metal bond is stronger in $Re_2(CO)_{10}$ than in $Mn_2(CO)_{10}$ [14,15], but contrasting behaviour is reported for $MnRe(CO)_{10}$ and $M_2(CO)_8(PPh_3)_2$ [3].

II. Experimental

$Mn_2(CO)_8(PPh_3)_2$ was synthesized from $Mn_2(CO)_{10}$ (Alfa Inorganics) and triphenylphosphine [16—21]. The identity of the product was confirmed by microanalysis (Found: C, 61.75; H, 3.62; calcd.: C, 61.53; H, 3.49%.) UV spectroscopy (see below), and IR spectroscopy.

$Re_2(CO)_8(PPh_3)_2$ was also prepared from $Re_2(CO)_{10}$ (Alfa Inorganics) and triphenylphosphine [22—25]. The microanalysis (found C, 47.27; H, 2.90; calcd.: C, 47.17; H, 2.70%), the UV absorption and the IR spectra were in agreement with the known spectra [3—5, 22—25].

$MnRe(CO)_8(PPh_3)_2$ was obtained by 12 h ultraviolet irradiation (80 W Osram) of a dry cyclohexane solution containing $MnRe(CO)_{10}$ and the ligand in stoechiometric quantities. The product was filtered off, recrystallized from benzene—hexane solution, and dried in vacuo (found C, 54.27; H, 3.55; calcd. C, 53.38; H, 3.03%). The identity of the compound was confirmed by its electronic spectra in CH_2Cl_2, IR spectroscopy (CO stretching frequencies in benzene (cm^{-1}): 1968(sh), 1954vs; solid KBr pellet: 1990(sh), 1948vs).

Electrochemical measurements were performed in dimethylformamide (DMF) and tetraethylammonium perchlorate (TEAP). The DMF was distilled from P_2O_5 before use, and the TEAP was twice recrystallized in methanol and dried in vacuo. Potentials were measured versus the saturated calomel electrode (SCE) electrically connected to the cell by a salt bridge containing the solution (DMF plus TEAP) (junction potential is estimated to 50 mV). The electrochemical methods involved were dc polarography, potentiostatic coulometry and cyclic voltammetry. The experimental procedures have been described previously [1,2,26—28]. UV spectra were recorded on a Beckman 1200 DB-G grating spectrophotometer, in CH_2Cl_2 and DMF as solvents. IR spectra were obtained with solid KBr pellets, or benzene solutions on a Beckman IR 12 apparatus.

III. Results

1. Electrochemistry

(a) On mercury electrode. In DMF and 0.1 *M* TEAP the disubstituted compounds $M_2(CO)_8(PPh_3)_2$, like $M_2(CO)_{10}$ [1,2], show well-defined polarographic waves whose half-wave potentials are listed in Table 1. For each compound, the limiting current is diffusion controlled (viz. linear relationships between the limiting current and, respectively, the electroactive species concentration and the square root of the mercury height). From the Ilkovic-Koutecky equation, the diffusion coefficients at 25°C are calculated (Table 1). The reduction processes are slow and the apparent rate constants at $E_{1/2}$ have been calculated [29] (Table 1). Noteworthy is that the half-wave potentials are more cathodic for $M_2(CO)_8(PPh_3)_2$ than for $M_2(CO)_{10}$ (ca. 200 mV). Potentiostatic coulometry

TABLE 1

POLAROGRAPHIC REDUCTION OF $M_2(CO)_{10}$ AND $M_2(CO)_8(PPh_3)_2$ ON MERCURY ELECTRODE IN DMF AND 0.1 *M* TEAP (M = Mn, Re)

Compounds	$Mn_2(CO)_{10}$ [2]	$Mn_2(CO)_8(PPh_3)_2$	$MnRe(CO)_{10}$ [2]	$MnRe(CO)_8(PPh_3)_2$	$Re_2(CO)_{10}$ [2]	$Re_2(CO)_8(PPh_3)_2$
$-E_{1/2}$ (V/SCE)	1.03	1.27	1.38	1.58	1.66	1.90
i_d (μA) (c 10^{-3} *M*/l)	3.7	2.8	3.8	2.4	3.2	3.9
D (cm^2 s^{-1}) at 25°C	9.4×10^{-6}	3.7×10^{-6}	9.7×10^{-6}	3×10^{-6}	7.1×10^{-6}	8.8×10^{-6}
$k_f(E_{1/2})$ (cm s^{-1})	1.0×10^{-3}	6.8×10^{-4}	1.1×10^{-3}	6.7×10^{-4}	1.0×10^{-3}	1.5×10^{-3}

TABLE 2

EXPERIMENTAL RESULTS OBTAINED FOR $M_2(CO)_{10}$ AND $M_2(CO)_8(PPh_3)_2$ IN LIQUID AND VAPOR PHASE

Compound	Liquid phase												Vapor phase
	Electrochemical oxydation/reduction				IR spectroscopy				UV spectroscopy				Metal—metal bond dissociation energies for $M_2(CO)_{10}$ (mass spectrometry)
	Cyclic voltametry on platinum electrode v = 0.1 V s^{-1}			Polarography on mercury	ν(M—M) (cm^{-1})		k (mdyn/Å)		$\sigma \to \sigma^*$ (nm)	ϵ (l mol^{-1} cm^{-1})	$\Delta(\sigma \to \sigma^*)$ (eV mol^{-1})	$Ep^a - Ep^c) - \Delta(\sigma \to \sigma^*)$	
	Ep^a (V/SCE)	$Ep^a - Ep^c$ (eV mol^{-1})	Ep^c (V/SCE)	$E^c_{1/2}$ (V/SCE)									ΔH (eV)
$Mn_2(CO)_{10}$	+1.80	6.44	−1.42	−1.03	160	159	0.59	0.41	342	20600	3.63	2.81	0.96
$MnRe(CO)_{10}$	+1.70	6.68	−1.64	−1.38	157	154	0.81	0.58	322	14900	3.85	2.83	2.67
$Re_2(CO)_{10}$	+1.65	7.28	−1.99	−1.66	122	120	0.82	0.79	310	16700	4.00	3.28	2.22
$Mn_2(CO)_8(PPh_3)_2$	+1.10	5.40	−1.60	−1.27	—	—	—	—	374	30600	3.31	2.09	—
$MnRe(CO)_8(PPh_3)_2$	+1.10	6.00	−1.90	−1.58	—	—	—	—	344	29600	3.60	2.40	—
$Re_2(CO)_8(PPh_3)_2$	+1.10	6.60	−2.20	−1.90	—	—	—	—	300	40000	4.14	2.46	—
Reference	this work				4	9	4	9	This work and ref. 3, 5, 6				11, 12

reveals that two Faradays are transferred per mole of $M_2(CO)_8(PPh_3)_2$, so that the electrochemical reduction can be written as follows:

$$M_2(CO)_8(PPh_3)_2 + 2e \rightarrow 2[M(CO)_4PPh_3]^-$$

Electroreduction then leads to metal—metal bond cleavage for both $M_2(CO)_{10}$ and $M_2(CO)_8(PPh_3)_2$ compounds.

If the system were reversible, the half-wave potentials would be related directly to this metal—metal bond energy. But although the standard potentials of the $M_2(CO)_{10}/M(CO)_5^-$ and the $M_2(CO)_8(PPh_3)_2/M(CO)_4PPh_3^-$ couples are not known, it is possible, as the kinetic parameters of electroreduction are similar, to try to correlate qualitatively $E_{1/2}$ with the energy level of the lowest vacant orbital. The overall algebraic sequence of the cathodic half-wave potentials is the following: $Mn_2(CO)_{10} > Mn_2(CO)_8(PPh_3)_2 > MnRe(CO)_{10} > MnRe(CO)_8(PPh_3)_2 > Re_2(CO)_{10} > Re_2(CO)_8(PPh_3)_2$.

Cyclic voltammetry on mercury electrode confirms (Fig. 1) that the reduction peaks Ep^c of $M_2(CO)_8(PPh_3)_2$ species are more cathodic than the corresponding $M_2(CO)_{10}$ peaks, and that the Ep^c values are in the order: $Mn_2(CO)_8(PPh_3)_2 > MnRe(CO)_8(PPh_3)_2 > Re_2(CO)_8(PPh_3)_2$. It has been verified that the ratio of the $M_2(CO)_8(PPh_3)_2$ cathodic peak currents to the square root of the scan rate (10—100 V s^{-1}) remains constant: thus the overall cathodic process is controlled by the rate of electron transfer, in full agreement with the results obtained from dc polarography.

(b) On platinum electrode. In DMF and 0.1 *M* TEAP, the ability of unsubstituted and of phosphine-substituted dimetallic carbonyls to be electrochemically reduced or oxidized on platinum has been examined by cyclic voltammetry.

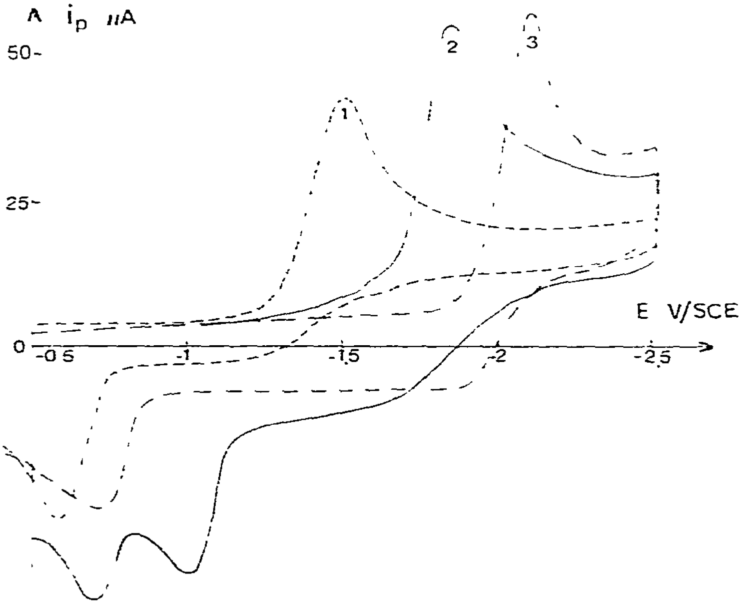

Fig. 1. Cyclic voltammetry of 10^{-3} *M* $M_2(CO)_8(PPh_3)_2$ in DMF + 0.1 *M* TEAP. Scan rate 100 V s^{-1}. Curve 1, $Mn_2(CO)_8(PPh_3)_2$; Curve 2, $MnRe(CO)_8(PPh_3)_2$; Curve 3, $Re_2(CO)_8(PPh_3)_2$.

The corresponding potentials of the cathodic and anodic peaks obtained by cyclic voltammetry at 0.1 V s^{-1} on platinum electrode are given in Table 2. The algebraic sequence of the cathodic peak potentials Ep^c parallels the sequence of the cathodic $E_{1/2}$ on mercury. For the anodic peak potentials Ep^a, due to the slow electron transfer the sequence can again only be interpreted qualitatively as a facilitated oxidation from $M_2(CO)_{10}$ to $M_2(CO)_8(PPh_3)_2$ (Table 2), as far as the kinetics of all the electro-oxidations are similar.

2. *Ultraviolet spectroscopy*

The electronic spectra of both $M_2(CO)_{10}$ and related $M_2(CO)_8(PPh_3)_2$ have been recorded at room temperature in the solvent (DMF) as used for the electrochemical measurements. The band maxima and the molar extinction coefficients are given in Table 2, particular attention being given to the near-UV absorption band whose assignment has been done recently by Levenson and Gray [5] to a $\sigma \rightarrow \sigma^*$ electronic transition involving orbitals of the metal—metal bond. This intense band shifts by replacement of axial CO by PPh_3, from 342 to 374 nm (Mn_2 compound) from 322 to 344 nm (MnRe compound) and surprisingly from 311 to 300 nm (Re_2 compound), even though the monosubstituted derivative $Re_2(CO)_9(PPh_3)$ is red-shifted to 320 nm [33].

3. *Discussion*

$M_2(CO)_{10}$. Experimental results concerning metal—metal bonded carbonyls are given in Table 2. These results were obtained either in solution (electrochemistry, IR, UV spectroscopy) or the gaseous phase (mass spectrometry). Unfortunately no IR nor mass spectrometry results are available of the metal—metal bond strength in $M_2(CO)_8(PPh_3)_2$ compounds. Consideration of the metal—metal stretching force constants, of the $\sigma \rightarrow \sigma^*$ band energies and of the oxidation—reduction potentials (Table 2) leads to the conclusion that the metal—metal bond energy decreases in $M_2(CO)_{10}$ according to the following sequence: $Re_2(CO)_{10} > MnRe(CO)_{10} > Mn_2(CO)_{10}$.

$M_2(CO)_8(PPh_3)_2$. In $Mn_2(CO)_{10}$ and $MnRe(CO)_{10}$ the replacement of two axial CO groups by PPh_3 decreases the energy (Δ) of the $\sigma \rightarrow \sigma^*$ maximum absorption band. Levenson and Gray [5] have shown that the energy of the $\sigma \rightarrow \sigma^*$ transition decreases as: $Mn_2(CO)_{10} > Mn_2(CO)_9PPh_3 > Mn_2(CO)_8(PPh_3)_2$. Apparently activation energies for kinetic processes involving Mn—Mn bond cleavage follow the same order [3].

In contrast in $Re_2(CO)_{10}$ the replacement of two axial CO groups by PPh_3 increases the energy of the $\sigma \rightarrow \sigma^*$ transition (Table 2), although the monosubstituted compound $Re_2(CO)_9PPh_3$ has a $\sigma \rightarrow \sigma^*$ transition less energetic than $Re_2(CO)_{10}$ [33]. For the rhenium derivatives, the energy of the $\sigma \rightarrow \sigma^*$ transition then decreases as: $Re_2(CO)_{10}(PPh_3)_2 > Re_2(CO)_{10} > Re_2(CO)_9PPh_3$.

Comparison of $M_2(CO)_{10}$ with $M_2(CO)_8(PPh_3)_2$. For all three dimetallic carbonyls, the cathodic half-wave potentials $E^c_{1/2}$ are cathodically shifted when two axial CO groups are replaced by PPh_3. This indicates that the energy of the lowest vacant orbital is increased by substitution of CO by PPh_3. Indeed a good indication of this specific effect of PPh_3 is given by the nearly constant cathodic shift (~ —0.2 V) observed from the non-substituted to the corresponding $(PPh_3)_2$ substituted carbonyl, irrespective of whether the dimetallic moiety is

Mn_2, Re_2, or MnRe. Such a cathodic shift induced by substitution of two CO's by more basic ligands in dimetallic compounds was noted by De Montauzon and Poilblanc [32] in the electroreduction of $Co_2(CO)_8$ and $Co_2(CO)_6L_2$: when replacing the two axial CO groups by more basic ligands L (L = $P(OPh)_3$, PPh_3, $P(OEt)_3$, PMe_2Ph, PMe_3, PEt_3) in $Co_2(CO)_8$, the half-wave reduction potentials are all the more cathodically shifted the more basic is the ligand L.

For $M_2(CO)_{10}$ compounds a correlation exists between the half-wave reduction potentials and the UV $\sigma \rightarrow \sigma^*$ transition energies [30,31] as shown in Fig. 2, but no simple correlation holds for $M_2(CO)_8(PPh)_3$.

The following two effects are then induced in the $M_2(CO)_8(PPh_3)_2$ molecules by the presence of the phosphine ligands: (a) The energy Δ ($\sigma \rightarrow \sigma^*$) of the transition $\sigma \rightarrow \sigma^*$ decreases from $M_2(CO)_{10}$ to $M_2(CO)_8(PPh_3)_2$ for Mn—Mn and Mn—Re, but increases from $Re_2(CO)_{10}$ to $Re_2(CO)_8(PPh_3)_2$; (b) The energy of the lowest vacant orbital σ^* increases from $M_2(CO)_{10}$ to $M_2(CO)_8(PPh_3)_2$ (M_2 = Mn_2, MnRe, Re_2).

As a consequence, the oxidation potentials (assuming no drastic change in the electrooxidation kinetics from Mn_2 to Re_2 compounds), must shift towards less positive values on substitution of two axial CO groups by two PPh_3 groups, the arithmetic value of this shift being (a) higher than the shift of the corresponding reduction potential, respectively, for $Mn_2(CO)_8(PPh_3)_2$ and $MnRe(CO)_8(PPh_3)_2$, but (b) smaller than the shift of the corresponding reduction potential for $Re_2(CO)_8(PPh_3)_2$.

This is verified for $Mn_2(CO)_8(PPh_3)_2$ and $MnRe(CO)_8(PPh_3)_2$ but not for $Re_2(CO)_8(PPh_3)_2$. Thus the changes in spectral and electrochemical properties between the $M_2(CO)_{10}$ compounds and their derivatives $M_2(CO)_8(PPh_3)_2$ cannot

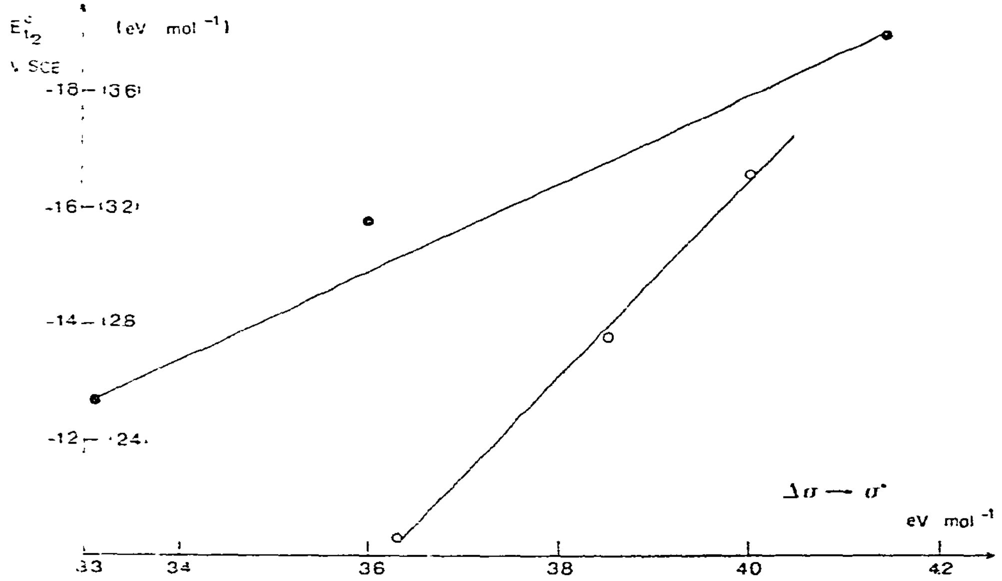

Fig. 2. Correlation between the half-wave reduction potentials (V/SCE) and the UV $\sigma \rightarrow \sigma^*$ transition energies involving orbitals from the metal—metal interaction (eV mol^{-1}). O, $M_2(CO)_{10}$ (M_2 = Mn_2, MnRe, Re_2); ●, $M_2(CO)_8(PPh_3)_2$.

be rationalized only in terms of the electron-donating character of PPh_3.

As the net result of the substitution of two axial CO groups by PPh_3 is to weaken the Mn—Mn and the Mn—Re bonds and to reinforce the Re—Re bond, as exemplified by the $\Delta(\sigma \rightarrow \sigma^*)$ and the oxidation reduction potentials, the electronic repulsion effects may very well dominate the $\sigma \rightarrow \sigma^*$ band shift [33].

However in each of the two series $M_2(CO)_{10}$ and $M_2(CO)_8(PPh_3)_2$, the electrochemical results parallel the spectral data very nicely, as exemplified by comparison of $(Ep^a - Ep^c)$ with $\Delta(\sigma \rightarrow \sigma^*)$.

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