Electrochemistry of Coordination Compounds. VI. Mixed 1,2-Bisdiphenyl-phosphinoethane Carbonyl Metal Anions Derived from Five-Coordinate Cobalt(I), Rhodium(I) and Iridium(I) Complexes

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The electrochemical behaviour of di-(1,2-bisdiphe-nylphosphinoethane)M(I) perchlorate (M = Co, Rh, Ir) has been investigated on the mercury electrode in acetonitrile under a carbon monoxide atmosphere. The reduction has been found to proceed via a two-electron step on the pentacoordinated CO adducts, thus providing evidence for the reversible addition of carbon monoxide also on the rhodium complex, and leading to anionic diphosphine carbonyl complexes.

Furthermore, the results showed that d^9 cobalt complex in the presence of carbon monoxide is highly unstable and a tentative interpretation of this behaviour is suggested. Reactions of the resulting metallo anions with electrophilic reagents, such as mercuric cyanide and triphenyltin chloride, afforded novel complexes containing metal–metal bonds.

Introduction

Recently we discussed the electrochemical reduction of the ionic d^8 complexes of cobalt, rhodium and iridium with 1,2-bisdiphenylphosphinoethane (DPE) as ligand, *i.e.* [M(DPE)$_2$]$^+$ [1,2]. The results strongly indicated the formation of a fugitive anion [M(DPE)$_2$]$^-$ able to undergo a fast reaction with the applied solvent to give [MH(DPE)$_2$]. Such a reactivity could be related to the weak π-acceptor properties of the phosphine ligands and, consequently, their substitution with better π-acceptors, like the CO molecule, could result in more stable anions. To achieve this goal, which was the pourpose of this work, the easiest method was the reduction of the complexes under CO atmosphere and, in fact, this procedure has been reported[3,4] as a simple and reliable method to obtain stable mixed carbonyl-phosphine metal anions useful as Intermediates in the synthesis of unusual organometallic compounds. Fur-thermore, since among the complexes we studied, the cobalt and iridium ones are known to coordinate the CO molecule, this allowed us to study the d^8 pentacoordinated systems which are related to an initial step in homogeneous catalysis.

Experimental Section

Materials

The complexes of the type [M(DPE)$_2$]ClO$_4$ were prepared by established methods[1,5,6]. The preparation of 1,2-bisdiphenylphosphinoethane (DPE) and the purification of acetonitrile have been reported in a previous paper[7]. All the chemicals employed were of reagent grade quality. Polarographic grade tetraethylammonium perchlorate, TEAP (R. P. C. Erba), was dried in vacuum at 75°C and used without further purification. All solutions contained 0.1*M* TEAP as supporting electrolyte. 99.999% argon was used for the removal of oxygen. 99.995% carbon monoxide, supplied by SIO (Italy), was employed in the experiments.

Apparatus and Procedure

The apparatus and the technique which were involved in the use of the polarographic apparatus, controlled potential coulometry and cyclic voltammetry have also been described previously[7].

The characteristics of the capillary were: m = 0.238 mg s^{-1} (air) at a mercury head of 47 cm. The dropping time was maintained at 1.0 s by forced fall of the drop.

Cyclic voltammetric polarograms were recorded, depending on the time scale of the experiment, either with the oscilloscope provided with a Polaroid camera attachment or with a Hewlett–Packard Model 7054A X–Y recorder. The surface area of the working electrode (H. M. E.) was in the range 1.36 to 1.40 sq.mm.

TABLE I. Infrared Spectra.

Complex	ν_{CO}, cm^{-1}
[Co(DPE)$_2$(CO)]$^+$	1925[a]
[Co(DPE)$_2$(CO)]$^-$	1765[a]
[Co(DPE)(CO)$_2$]$^-$	1785, 1845[a]
[Co(DPE)(CO)$_3$]$^-$	1830, 1925[a]
[Co(DPE)(CO)$_2$]$_2$Hg	1895, 1935[b]
[Co(DPE)(CO)$_2$(SnPh$_3$)]	1900, 1950[b]
[Ir(DPE)$_2$(CO)]$^+$	1945[a]
[Ir(DPE)$_2$(CO)]$^-$	1775[a]
[Ir(DPE)(CO)$_2$]$^-$	1790, 1845[a]
[Ir(DPE)(CO)$_2$(SnPh$_3$)]	1920, 1960[b]
[Rh(DPE)$_2$(CO)]$^+$	1960[a]
[Rh(DPE)(CO)$_2$]$^-$	1805, 1860[a]
[Rh(DPE)(CO)$_2$(SnPh$_3$)]	1935, 1970[b]

[a] Acetonitrile solution. [b] KBr disk.

In the polarographic measurements the concentration of the depolarizer was in the range 2×10^{-4}–$2 \times 10^{-3} M$, in the coulometric ones varying from 5×10^{-3} to $2 \times 10^{-2} M$.

Unless otherwise stated the temperature was fixed at $25.0 \pm 0.1°C$. Infrared spectra were recorded in KBr disks or in solution on a Perkin–Elmer Model 457 grating spectrometer. Positions of the infrared bands assigned to the CO stretchings are given in Table I.

Elemental analysis was performed by the Microanalytical Laboratory of the Pharmaceutical Chemistry Institute of the University, Padua. The results are collected in Table II.

Results

Cobalt System

The solution of [Co(DPE)$_2$]$^+$, generated in the polarographic cell[1] starting from [CO(DPE)$_2$]$^{2+}$, when saturated with CO changes from brown to yellow, typical of the formation of [Co(DPE)$_2$(CO)]$^{+}$[8] (ν_{CO} = 1925, CH$_3$CN soln.). In the same time a single two-electron, reversible wave ($E_{1/2}$ = −1.30V), resulting from the two reversible one-electron steps of the decarbonylated Co(I) complex, appeared in the polarogram (Figure 1).
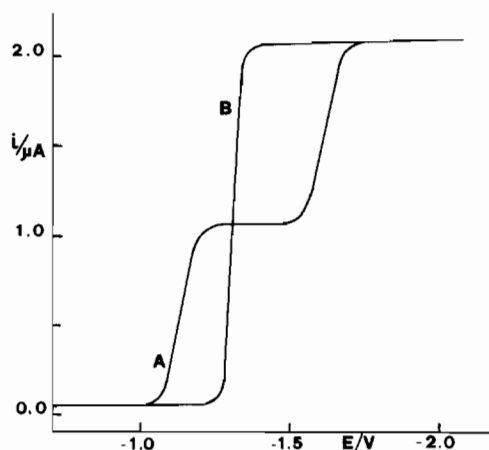

Figure 1. Polarograms of $1.2 \times 10^{-3} M$ [Co(DPE)$_2$]$^+$ (wave A) and [Co(DPE)$_2$(CO)]$^+$ (wave B) in $0.1 M$ TEAP, CH$_3$CN soln. at 25.0°C.

Exhaustive controlled potential electrolysis in the potential range of the plateau required two mol of electrons per mol of depolarizer, giving a pale yellow solution. The IR spectrum of this solution showed two strong bands in the carbonyl region, 1925 and 1830 cm^{-1}, different from those of [Co(DPE)(CO)$_2$]$^-$[9], but quite identical (1925 and 1830 cm^{-1}) with those of an authentic sample of [Co(PPh$_3$)(CO)$_3$]$^-$[10]. By evaporation of the solvent under reduced pressure, and subsequent extraction with benzene one mol of DPE, m.p. 143°C, per mol of cobalt was recovered.

In view of the particular stability of [Co(DPE)$_2$(CO)]$^+$, we repeated the electrolysis of the carbonyl adduct without free CO in solution, $i.e.$ under argon atmosphere. In this case a two-electron reduction is still obtained, but the product was unstable as showed by the fading of the orange colour in the time. In order to identify such a product, some experiments were performed at −30°C. At this temperature the electrolysis afforded a stable orange solution whose polarogram showed a two-electron anodic wave with the same half-wave potential as the starting compound. The IR spectrum of this solution exhibited a single strong band at 1765 cm^{-1}, attributable to a stretching mode of CO bonded in a low-valent anionic complex[11]. Further-

TABLE II. Elemental Analysis.

Compound	Calculated %				Found %			
	C	H	P	O	C	H	P	O
[Co(DPE)(CO)$_2$]$_2$Hg	54.80	3.94	10.10	5.21	55.11	4.04	9.90	5.40
[Co(DPE)(CO)$_2$(SnPh$_3$)]	63.99	4.55	7.17	3.71	62.97	4.27	7.00	4.03
[Ir(DPE)(CO)$_2$(SnPh$_3$)]	55.44	3.94	6.22	3.21	55.36	4.01	6.17	3.27
[Rh(DPE)(CO)$_2$(SnPh$_3$)]	60.89	4.33	6.83	3.53	61.10	4.45	7.04	3.30

more, by adding with a gas syringe to the solution the equivalent amount of carbon monoxide the colour changed from orange to lemon-yellow, while one mol of free DPE per mol of cobalt precipitated (at $-30°$C, in CH_3CN, DPE is sparingly soluble). The IR spectrum was now identical with that of the solution of an authentic sample of $[Co(DPE)(CO)_2]^-$ [9]. The identity of this anion has been, furthermore, checked by reaction with $Hg(CN)_2$ and $ClSnPh_3$ which caused precipitation of the known $Hg[Co(DPE)(CO)_2]_2$,[9] and the previously unreported $[Ph_3SnCo(DPE)(CO)_2]$, respectively. A further addition of carbon monoxide to the solution of $[Co(DPE)(CO)_2]^-$ resulted in the obtaining of the previously described compound (see above). This last result together with the infrared spectrum strongly suggests for this species the formulation $[Co(DPE)(CO)_3]^-$, with DPE acting as monodentate ligand. Attempts to isolate this species as $[Ph_3\cdot SnCo(DPE)(CO)_3]$ or as $Hg[Co(DPE)(CO)_3]_2$ failed. Furthermore, the removal of the solvent under reduced pressure afforded the recovery of the previously described dicarbonylated complexes.

Iridium System

When CO is bubbled into the orange solution of $[Ir(DPE)_2]^+$ a fast discharge of the colour is noted, and the known $[Ir(DPE)_2(CO)]^+$ is formed[12] (ν_{CO} = 1945, CH_3CN soln.). Since it is known that the CO uptake is reversible[13], we investigated the electrochemical behaviour of the complex under CO atmosphere.

The two-electron reduction wave, unlike that of the decarbonylated species[2], was irreversible with a shift of half-wave potential from -1.70V (decarbonylated species[2]) to -1.95V (carbonylated species) (Figure 2).

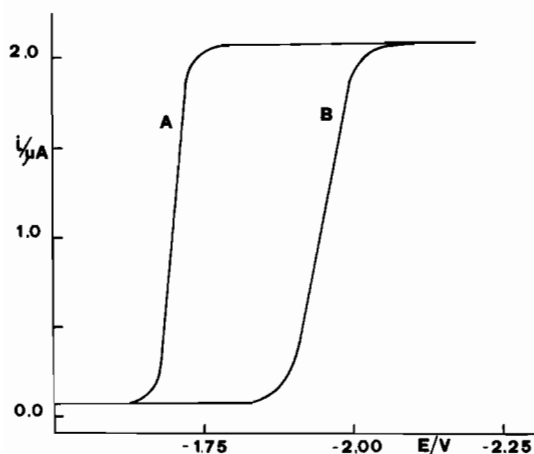After electrolysis (two mol of electrons per mol of iridium) the infrared spectrum of the colourless solution indicated the absence of the starting complex (no band at 1945 cm^{-1}). Two strong carbonyl bands, observed at 1845 and 1790 cm^{-1}, are in the low-frequency region expected for carbonyl anion complexes[11].

The subsequent addition to the electrolytical cell of $ClSnPh_3$ gives a white crystalline precipitate, identified by elemental analysis and IR spectrum as $[Ph_3SnIr(DPE)(CO)_2]$. Furthermore, the evaporation under reduced pressure of the solvent allowed the recovery of the stoichiometric amount of extra DPE.

It is inferred from the infrared spectrum and chemical reaction that the species in the reduced solution is the iridium(–I) carbonyl anion $[Ir(DPE)(CO)_2]^-$, analogous to the previously described cobalt one. Since in the cobalt system it was possible to verify the primary formation of a monocarbonylated anion which underwent a subsequent fast reaction with the carbon monoxide to afford $[Co(DPE)(CO)_2]^-$ (see above) we tried to do the reduction of $[Ir(DPE)_2(CO)]^+$ without free CO in solution. At low temperature ($-30°$C) the loss of the coordinated CO is undetectable and, in such conditions, the two-electron, irreversible reduction gives an orange solution whose IR spectrum showed a single carbonyl band at 1775 cm^{-1}, in accordance with the presence of a monocarbonylated metallo anion. Bubbling CO into the orange solution discharged the colour and afforded the previously identified $[Ir(DPE)(CO)_2]^-$ together with the precipitation of the released DPE.

Rhodium System

The polarographic pattern of $[Rh(DPE)_2]^+$ in the presence and in the absence[2] of CO is quite different, in the former case a shift of the polarographic wave of 50 mV towards more positive potentials and a modification from reversible shape to an irreversible one being noted (Figure 3). This result was hard to under-
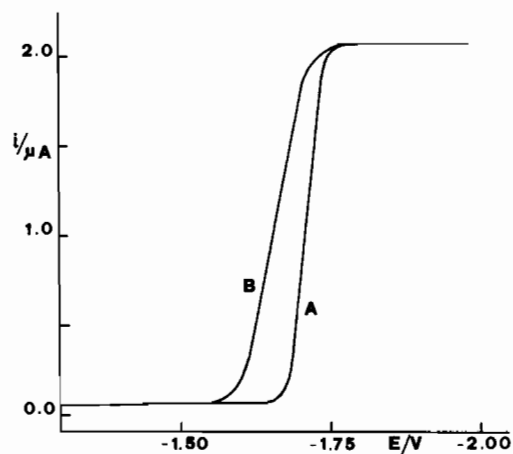

Figure. 2. Polarograms of $1.3 \times 10^{-3}M$ $[Ir(DPE)_2]^+$ (wave A) and $[Ir(DPE)_2(CO)]^+$ (wave B) in $0.1M$ TEAP, CH_3CN soln. at $25.0°$C.

Figure 3. Polarograms of $1.2 \times 10^{-3}M$ $[Rh(DPE)_2]^+$ in $0.1M$ TEAP, CH_3CN soln. at $25.0°$C: under argon (wave A) and under carbon monoxide (wave B).

stand since the lack of coordination of the CO molecule to the rhodium(I) complex was known[13].

Exhaustive controlled potential electrolysis under CO atmospheric pressure showed: i) the uptake of two mol of electrons per mol of depolarizer; ii) no formation of the metal hydride previously found in the absence of CO^2; iii) a fading of the starting yellow colour to a very pale-yellow one; iv) the presence in the infrared spectrum of the reduced solution of two bands at 1805 and 1860 cm^{-1}; v) the release of one mol of DPE *per* mol of complex. Furthermore the addition of one mol equivalent of $ClSnPh_3$ resulted in the precipitation of a light yellow crystalline product identified by elemental analysis and I.R. spectrum as $[Ph_3SnRh(DPE)(CO)_2]$.

Such behaviour could be rationalized in terms of a chemical reaction of carbon monoxide with the reduction product, *viz.* $[Rh(DPE)_2]^{-2}$, to give $[Rh(DPE)(CO)_2]^-$, this interpretation being, however, in contrast with the polarographic response. In fact an irreversible chemical reaction following a reversible charge transfer (EC mechanism) implies an anodic shift of the wave, the reversible shape of the same being not affected.

To shed some light on these discrepancies we did detailed cyclic voltammetric experiments, particularly suitable to characterize complex reaction sequences. The voltammetric profile is very sensitive to the rate of potential scan, as shown in Figures 4, 5, 6. It appears,
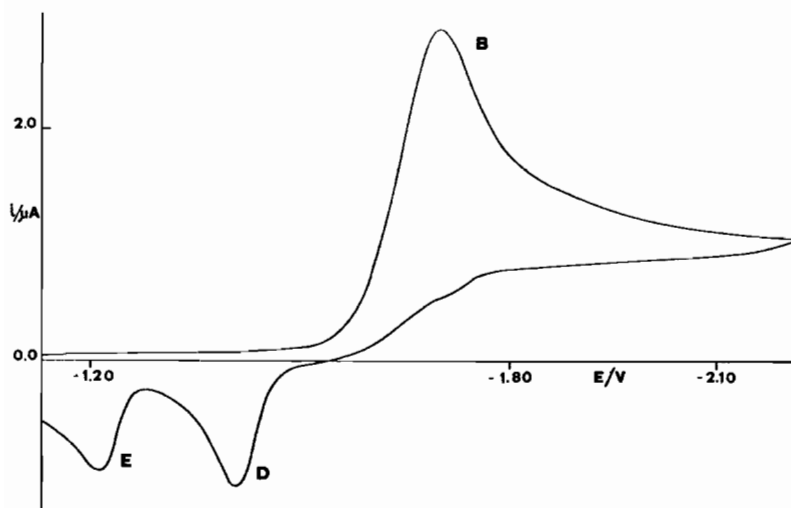

Figure 4. Cyclic voltammetric curve in a $0.7 \times 10^{-3} M$ $[Rh(DPE)_2]^+$, $0.1 M$ TEAP, CH_3CN soln. saturated with CO at $25.0°C$; scan rate $= 0.033$ V s^{-1}.
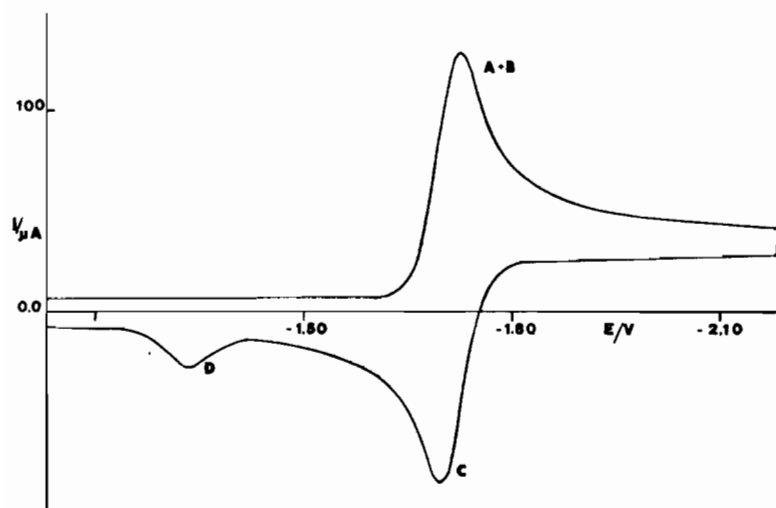

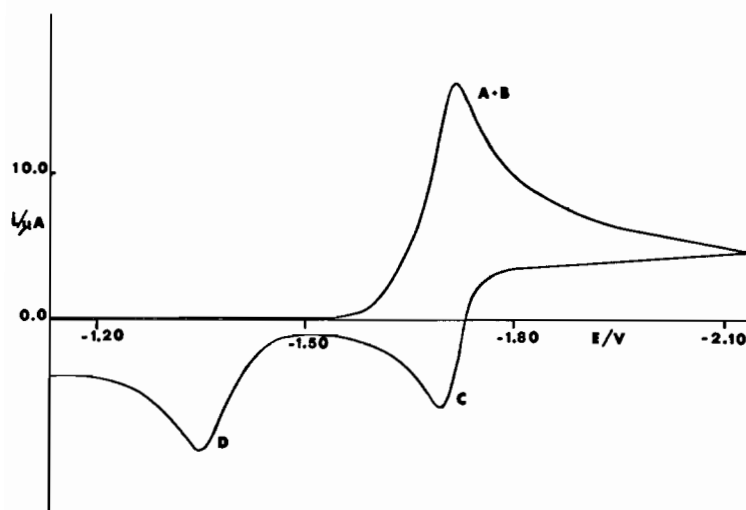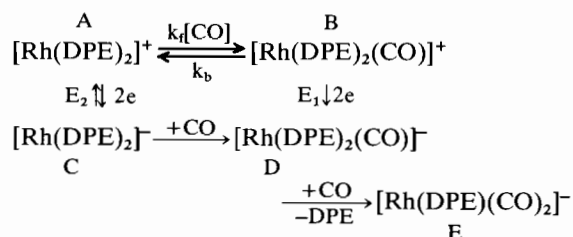Figure 5. Same as figure 4; scan rate $= 40.0$ V s^{-1}.

Figure 6. Same as figure 4; scan rate $= 1.0$ V s^{-1}.

in fact, that only a single two-electron cathodic response, irreversible at low scan rates, but approaching that of reversible charge transfer as the scan rate is increased, is observed. As the potential is returned to anodic values, three additional anodic responses (C, D, E), may be observed, depending on the rate of voltage scan. This behaviour, taking into account that: i) peak C is the oxidation of $[Rh(DPE)_2]^-$ back to $[Rh(DPE)_2]^{+2}$, ii) peak E is ascribed to the oxidation of the final product, *i.e.*, $[Rh(DPE)(CO)_2]^-$, as supported by cyclic voltammetric experiments performed in solutions electrolyzed under CO, could be accounted for by the following reaction scheme:

$$\underset{A}{[Rh(DPE)_2]^+} \underset{k_b}{\overset{k_f[CO]}{\rightleftharpoons}} \underset{B}{[Rh(DPE)_2(CO)]^+}$$

$$E_2 \updownarrow 2e \qquad\qquad E_1 \downarrow 2e$$

$$\underset{C}{[Rh(DPE)_2]^-} \xrightarrow{+CO} \underset{D}{[Rh(DPE)_2(CO)]^-}$$

$$\xrightarrow[-DPE]{+CO} \underset{E}{[Rh(DPE)(CO)_2]^-}$$
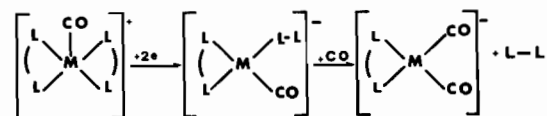
The CO adduct, B, is assumed to be reduced at a little more anodic potential than the parent one A.

Thus, in the electrode process the reduction of both A and B in equilibrium takes place. However, if the time scale of the experiments is great relative to the rate of the chemical reaction, the response is that of the uncomplicated irreversible reduction of B to D followed by the partial conversion of D to E (Figure 4). At the opposite extreme in rate of the potential scan no significant conversion of A to B can take place: under such conditions the voltammetric profile is determined by the equilibrium concentrations of the reducible species (Figure 5). At intermediate conditions both reductions of A and B are operating with a

ratio depending on the kinetic parameters, k_f and k_b, and on the pressure of carbon monoxide (Figure 6). Furthermore, the presence of peak D also at the highest scan rate (Figure 5), where presumably the experiment is over before significant conversion of A to B and/or C to D can occour, implies the existence of detectable amount of B in equilibrium with A. Thus the presence in solution of complex B must be recognized as supporting the proposed reaction scheme. In fact the infrared spectrum of a concentrated $(6 \times 10^{-2}M)$ solution of $[Rh(DPE)_2]^+$, when saturated with carbon monoxide (1 atm.), reveals a carbonyl band at 1960 cm^{-1}, providing additional evidence for the formation of a carbonylated rhodium(I) complex. The fast disappearance of the CO band when the solution is swept with argon, is consistent with the reversibility of the CO addition.

Discussion

Some points of interest follow from the experimental results. First of all, the previously found differences between lighter and heavier elements of the same triad[1] disappear in such a way that the polarographic reduction pattern of the d^8 pentacoordinated CO adducts of cobalt, rhodium and iridium can be accounted for by a common scheme (L–L = DPE):

$$\left[\begin{array}{c} L \\ (\\ L \end{array} \underset{L}{\overset{CO}{>}} M \underset{L}{\overset{L}{<}} \right]^+ \xrightarrow{+2e} \left[\begin{array}{c} L \\ (\\ L \end{array} > M \overset{L-L}{<} \right]^- \xrightarrow{+CO} \left[\begin{array}{c} L \\ (\\ L \end{array} > M \underset{CO}{\overset{CO}{<}} \right]^- + L-L$$

with the electrochemical step reversible for the cobalt complex and irreversible for the rhodium and iridium

ones. This different behaviour strongly suggests that the activation energy of the processes is in the order $Co < < Rh$ and Ir. It is well known that such an energy is related to that required for the electronic rearrangement of the depolarizer before or in the course of the electrode process to vacate a low-lying orbital for the direct acceptance of electrons[14]. Consequently, the cobalt complex must possess, probably in an excited state very close to the ground one, such a low-lying empty orbital, the lowest vacant one in the isoelectronic congeners being of relatively high energy. This conclusion can be rationalized in at least two ways. The pentacoordinated species could have different structures, ranging between trigonal bipyramidal and square pyramidal geometries which involve a different energy level ordering. Alternatively this trend could arise from the increasing σ bonding in the order $3d < 4d < 5d$, with the parallel destabilization of the σ antibonding empty orbital.

Furthermore, from the two-electron uptake, common to the three metals, emerges the high instability also of the cobalt d^9 configuration, when a CO molecule is present as a ligand. In fact, previously we found the d^9 $[Co(DPE)_2]$ as the product of the one-electron reduction of $[Co(DPE)_2]^+$ [1]. In supposing that such an instability could be related to the presence of a carbonyl group in the complex we did the reaction between $[Co(DPE)_2]$ and CO. Quite instantaneously the reaction went to completion and the two products in 1:1 ratio were identified polarographically and by i.r. spectra as $[Co(DPE)(CO)_3]^-$ and $[Co(CO)(DPE)_2]^+$. The promotion of the disproportionation by the carbon monoxide is not an unusual fact[15]. However, almost in our case, such a finding could be accounted for in considering that in CH_3CN the very fast equilibrium:

$$2[Co(DPE)_2] \rightleftarrows [Co(DPE)_2]^+ + [Co(DPE)_2]^-$$
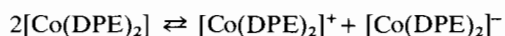
is operating[1] with the cathionic and anionic partners able to react with CO giving $[Co(CO)(DPE)_2]^+$ and carbonylated anionic species, respectively.

As far as the rhodium and iridium complexes chemical behaviours are concerned, some other comments have to be made.

Since $[Rh(DPE)_2]^+$ and $[Ir(DPE)_2]^+$ were found to possess the same electron uptake ability[2], one would expect perhaps the same interaction with the CO ligand which is, however, not observed. In fact the iridium complex forms an isolable adduct with carbon monoxide while the rhodium one possesses only a small amount of adduct in equilibrium with the decarbonylated species.

Similar different behaviour between rhodium and iridium has been noted[16], but not clearly understood

since i) the role of the metal with the "amphoteric" (in Vaska's sense) CO ligand cannot be defined at present[16], ii) different kinetic factors for the two metal complexes could be implied.

Finally it can be noted also that a single CO group present in the d^{10} species is not enough to stabilize it. In such a case the anion still reacts either rapidly with extra CO if present, or slowly with the applied solvent to form, quite probably, carbonylated hydridic compounds as showed by the infrared spectra of the crude and intractable products obtained after removal of the solvent (bands in the M–H region and in the CO stretching region).

When two CO groups are present in the d^{10} anionic complex the resulting product is perfectly stable as proved by polarographic and IR measurements as a function of time. The basic character of these d^{10} anionic complexes, as well as that of the isoelectronic neutral ones[3], is manifest in the reaction with Lewis acids such as mercuric cyanide or triphenyltin chloride. These reactions afford isolable products which apparently contain metal–metal bonds, and support the electrochemical method as a useful route to obtain such compounds of considerable current interest.

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