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POLAROGRAPHIC BEHAVIOUR OF π-ALLYLIC COMPLEXES OF TRANSITION METALS

II. π-ALLYLTRICARBONYLCOBALT AND SOME PHOSPHINIC DERIVATIVES

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Summary

The polarographic reduction in acetonitrile (ACN) of π-$C_3H_5Co(CO)_3$ and of the phosphinic derivatives π-$C_3H_5Co(CO)_2L$ [L = $P(OC_6H_5)_3$, $P(OCH_2)_3$-CC_2H_5, $P(C_6H_5)_3$, $P(OC_2H_5)_3$, P-n-Bu_3, $P(C_6H_{11})_3$] is reported and the reduction mechanism is discussed. The dependence of the $E_{1/2}$ of the complexes on the properties of the ligands is analysed, and a linear plot of $E_{1/2}$ vs. ΔHNP of the ligands is observed. The pseudo first-order rate constants for the reduction of the complexes with $NaBH_4$ in ACN are reported.

Introduction

We previously studied the polarographic behaviour of complexes of the type π-$C_3H_4XFe(CO)_2NO$ as part of a programme concerned with the characterisation of the electrochemical behaviour of π-allylcarbonyl— and π-allylcarbonylnitrosyl—transition metal complexes [1]. We found that electronic change was localised in the Fe—allyl bond, and we discussed the effects of the substituent X on the reduction potential and the reduction mechanism. We now report a similar study of the complex π-$C_3H_5Co(CO)_3$, and some of its phosphinic derivatives of formula π-$C_3H_5Co(CO)_2L$. The object was to obtain information about the effect of the metal and the phosphinic ligands on the reduction mechanism, and to identify the nature of the final products.

Experimental

(a) Polarography

Conventional d.c. polarography was carried out in acetonitrile (ACN), purified as described in ref. 2, with tetraethylammonium perchlorate (0.1 *M* solution) as the supporting electrolyte. A three electrode Amel Mod. 462 polarograph was employed using a saturated calomel electrode as the reference electrode.

The test solutions, thermostatted at 22° C, were degassed with ACN-saturated argon before measurements. A slow stream of argon was passed over the solutions during measurements.

(b) Coulometry

The number of electrons involved in the reduction step (*n*) was determined by controlled-potential coulometry. These measurements were carried out both at a mercury pool electrode and at a platinum sheet in a solution stirred by a magnetic stirrer. Coulometric runs were stopped at intervals to perform polarographic and spectrophotometric (IR) checks. Solutions were degassed with argon and in some experiments saturated with carbon monoxide.

(c) Kinetic measurements

The reactions between π-$C_3H_5Co(CO)_2L$ and $NaBH_4$ were carried out by adding a known quantity of complex to a saturated solution of $NaBH_4$ in the presence of solid $NaBH_4$ in ACN at 22° C. The solutions were continuously stirred during the reduction. The rate constants were measured by monitoring both the decrease in intensity of the IR C—O stretching mode at higher frequency of π-$C_3H_5Co(CO)_2L$ and the increase in intensity of the analogous band, at lower frequency, of the $Co(CO)_3L^-$ product. The rate constants so obtained were reproducible within the expected limits of experimental error.

(d) Materials

The preparation and purification of π-$C_3H_5Co(CO)_3$ was carried out as described in ref. 3. The monosubstituted complexes π-$C_3H_5Co(CO)_2L$ [L = $P(C_6H_{11})_3$, P-n-Bu_3, $P(OC_2H_5)_3$, $P(C_6H_5)_3$, $P(OCH_2)_3CEt$, and $P(OC_6H_5)_3$] were prepared by treating equimolar quantities of π-$C_3H_5Co(CO)_3$ and ligand L in ethyl ether [4]. Solid complexes were purified by recrystallisation from dichloromethane/n-pentane mixtures, and liquids by fractional distillation. Identification of the products of both chemical and electrochemical reduction was carried out by comparison of their IR spectra with those of authentic samples [5, 6]. Other experimental details are described in ref. 1.

Results and discussion

(a) π-Allyltricarbonylcobalt

π-$C_3H_5Co(CO)_3$ is reduced at the dropping mercury electrode in a single bielectronic wave ($E_{1/2}$ —1.601 V), the limiting current of which is proportional to the concentration of the depolariser in a large concentration range (10^{-4} — 10^{-2} *M*). The wave has diffusion character; a plot of limiting current against the square root of the mercury column height is linear and passes through the origin.

The number of electrons consumed during the reduction was determined by comparing the diffusion current with those obtained for the complexes $Fe(CO)_5$, $Mn_2(CO)_{10}$ and π-$C_3H_5Fe(CO)_2NO$, which all give a single two electron diffusion wave.

Cyclic voltammetric tests carried out up to a scan rate potential of 5 V/sec

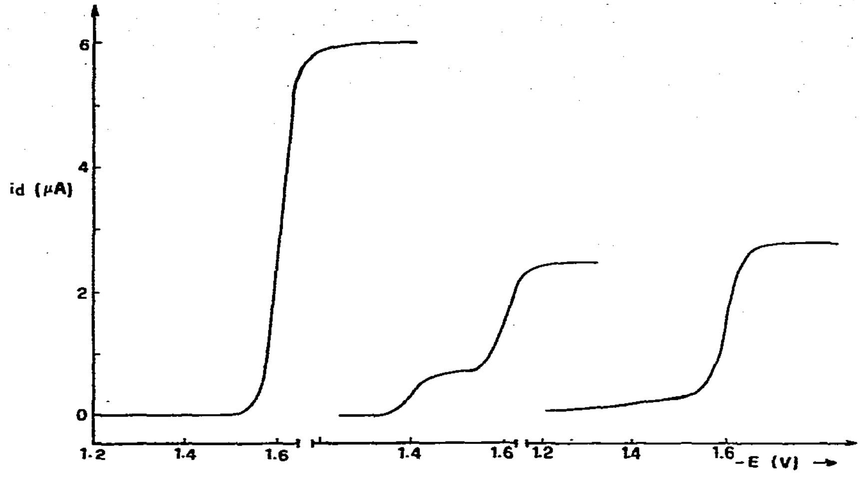


Fig. 1. Coulometric reduction of π-$C_3H_5Co(CO)_3$ in argon atmosphere at —1.7 V. (a) Polarogram of the initial solution, (b) Polarogram of the solution after partial reduction, (c) Polarogram of the solution after partial reduction and stirring.

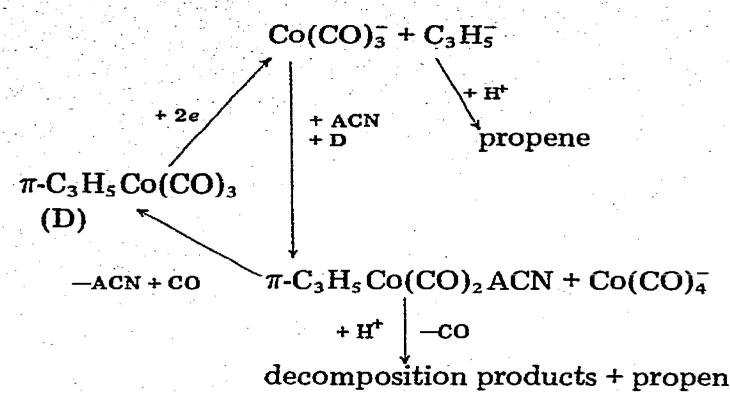
clearly show that the process involved is irreversible. Logarithmic analysis of the polarographic wave confirms this, and allows a value for αn of 1.57 to be calculated. This unusually high value (αn is usually < 1) gives further support to the suggestion that n must be greater than one, and is most probably 2 [7]. Both the chemical reduction with $NaBH_4$ and the coulometric reduction give rise to the same products. These, characterised via IR spectra, were found to be propene and $Co(CO)_4^-$.

In polarograms of partially electrolysed solutions, in addition to a decrease in the reduction wave of the complex π-$C_3H_5Co(CO)_3$, a new cathodic wave appears at a less negative potential ($E_{1/2}$ —1.41 V). The latter rapidly disappears on bubbling argon through the solution (more slowly if the solution is shaken vigorously) with simultaneous increase in the height of the cathodic wave of the depolariser (see Fig. 1).

The number of electrons (n) transferred during the reduction of π-C_3H_5-$Co(CO)_3$ is little higher than one until a small percentage of complex has been reduced and then increases with increase in the reduction percentage. The average value, referred to complete reduction of the depolariser, is a little lower than 2.

The formation of a cathodic wave at —1.41 V is not observed in the coulometric reduction carried out under an atmosphere of carbon monoxide, and n has the same behaviour as described above with the difference that it rises from higher initial values. In two typical experiments, carried out under argon with more or less equal initial concentrations of complex, the n values were 1.27 and 1.67, respectively, for a ca. 30% reduction of the complex. In addition, the amount of final reduction product, $Co(CO)_4^-$, corresponds to a yield of ca. 50% referred to starting complex for reductions carried out under argon, whilst the yield was always higher in reductions carried out under carbon monoxide.

The above experimental observations allow the reduction mechanism (1)



(1)

to be proposed. As already found for the reduction of π-$C_3H_5Fe(CO)_2NO$ [1], the first stage corresponds to a transfer of two electrons into an orbital of the metal—allyl bond, leading to homolytic cleavage of this bond. The species $Co(CO)_3^-$, so formed, may then give the final product, $Co(CO)_4^-$, via two different pathways: reaction with itself and/or reaction with the starting complex. A sensible contribution of the first pathway can be ruled out since the concentration of the species $Co(CO)_3^-$ is always very small (in fact, it cannot be experimentally observed during the runs, differently from the case of π-$C_3H_5Fe(CO)_2NO$ [1]). The reaction between $Co(CO)_3^-$ and π-$C_3H_5Co(CO)_3$ produces, in addition to $Co(CO)_4^-$, a polarographically reducible species ($E_{1/2}$ —1.41 V), for which we propose the structure π-$C_3H_5Co(CO)_2$. This species, possibly stabilized by the solvent, may either react with CO to give the starting complex (as observed experimentally) or decompose. The electron-deficient nature of such an intermediate is consistent with the fact that its reduction potential is less negative than that of π-$C_3H_5Co(CO)_3$.

(b) Monosubstituted derivatives of π-$C_3H_5Co(CO)_3$

As for the parent compound, monosubstituted complexes of the type π-$C_3H_5Co(CO)_2L$ are irreversibly reduced at the DME, giving rise to a bielectronic wave which is diffusive in character. Coulometric reductions at controlled potential give $n = 1$. However, in contrast to the reduction of π-C_3H_5-$Co(CO)_3$, no intermediate could be observed by polarographic or spectrophotometric methods.

The products of electrochemical and chemical ($NaBH_4$) reductions are propene and the complexes $Co(CO)_3L^-$ and $Co(CO)_4^-$. The ratio $[Co(CO)_3L^-]/[Co(CO)_4^-]$ is usually high and for all cases is considerably influenced by the nature of the ligand, L (basicity and π-backdonation capacity).

On the basis of these data, the reduction mechanism (2) is proposed. This

$$\pi\text{-}C_3H_5Co(CO)_2L \xrightarrow[+\,H^+]{+\,2e} Co(CO)_2L^- + C_3H_6$$

$$Co(CO)_2L^- + \pi\text{-}C_3H_5Co(CO)_2L \begin{cases} \longrightarrow Co(CO)_3L^- + C_3H_6 + \text{other products} \\ \longrightarrow Co(CO)_4^- + C_3H_6 + \text{other products} \end{cases} \quad (2)$$

mechanism differs from that previously proposed for π-$C_3H_4XFe(CO)_2NO$ complexes [1] only in that, since the number of electrons consumed in the reduc-

TABLE 1

ΔHNP OF THE PHOSPHINIC LIGANDS; IR CO STRETCHING FREQUENCIES AND $E_{1/2}$ AND PSEUDO-FIRST ORDER REDUCTION RATE CONSTANTS (k) FOR THE π-$C_3H_5Co(CO)_2L$ COMPLEXES; IR CO STRETCHING FREQUENCIES FOR THE $Co(CO)_3L^-$ COMPLEXES

Ligand L	ΔHNP	π-$C_3H_5Co(CO)_2L$			$Co(CO)_3L^-$		k (sec^{-1})
		$-E_{1/2}$ (Volt)	$\nu'(CO)$ (cm^{-1})	$\nu''(CO)$ (cm^{-1})	$\nu'(CO)$ (cm^{-1})	$\nu''(CO)$ (cm^{-1})	
CO		1.601	2058	1988	1893		
$P(OPh)_3$	875	1.836	2009	1955	1962	1873	3.8×10^{-3}
$P(OCH_2)_3CEt$	665	1.934	2009	1950	1950	1858	2.1×10^{-3}
PPh_3	573	1.962	1985	1928	1925	1837	1.3×10^{-3}
$P(OEt)_3$	420	2.098	1992	1936	1942	1850	$\sim 1 \times 10^{-6}$
P-n-Bu_3	300	2.174	1973	1912	1915	1822	6.7×10^{-5}
$P(C_6H_{11})_3$	33	2.199	1969	1908	1909	1815	9.4×10^{-5}

[a] ΔHNP indicates the semi-neutralization potentials, referred to that of *N,N'*-diphenylguanidine as standard, in nitromethane as solvent.

tion is one (and remains constant with variation in the percentage of substance reduced), any reaction involving interaction of the intermediate with itself may be excluded.

The measured rate constants for chemical reductions with $NaBH_4$ are first order. This is in agreement with the above mechanism if it is assumed that the concentration of $Co(CO)_2L^-$ obeys the stationary state approximation. Under these conditions, $v = k[\pi\text{-}C_3H_5Co(CO)_2L]\,[NaBH_4]$, and in saturated $NaBH_4$ solution the kinetics become pseudo first order.

Table 1 shows the C—O stretching frequencies for the complexes π-C_3H_5-$Co(CO)_2L$ and $Co(CO)_3L^-$ in ACN together with half-wave potentials, pseudo first order rate constants, and ΔHNP values [8] for the ligand L (which give a measure of ligand basicity).

The variations in the C—O stretching frequencies of the $Co(CO)_3L^-$ complexes parallel those for the π-$C_3H_5Co(CO)_2L$ ones. This indicates that, as for most carbonyl complexes, the position of the CO frequency is influenced

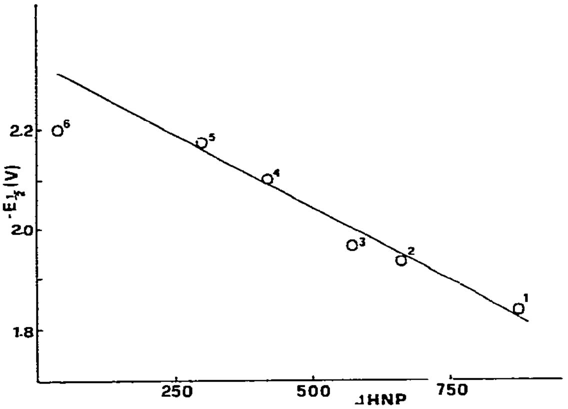


Fig. 2. $E_{1/2}$ of the π-$C_3H_5Co(CO)_2L$ complexes vs. ΔHNP of the phosphinic ligands L [L = $P(OC_6H_5)_3$ (1), $P(OCH_2)_3CC_2H_5$ (2), $P(C_6H_5)_3$ (3), $P(OC_2H_5)_3$ (4), P-n-Bu_3 (5), $P(C_6H_{11})_3$ (6)].

by the capacity of the ligand L to accept electrons in the empty anti-bonding orbitals of the phosphorus [9].

A plot of half-wave potential against ΔHNP is shown in Fig. 2. Apart from $L = P(C_6H_{11})_3$, a straight line is obtained. We deduce that the half-wave potential is predominantly influenced by the capacity of the ligand to transfer σ electrons to the metal ion. An increase of electron density on the metal ion would then shift $E_{1/2}$ towards more negative values.

The rate constants show a similar, though not linear behaviour, apart from that for $P(OC_2H_5)_3$, for which there is a very low value for the rate constant.

Conclusions

The results obtained to date for the complexes π-$C_3H_5Fe(CO)_2NO$, π-$C_3H_5Co(CO)_3$ and their derivatives π-$C_3H_4XFe(CO)_2NO$ and π-$C_3H_5Co(CO)_2L$ suggest that the same mechanism of reduction applies in all these cases. Depending on the nature of the metal ion and substituent groups present, kinetic factors render some of the steps of the general mechanism observable or otherwise, which means that reaction steps which have not come to light experimentally cannot altogether be excluded. Other related complexes must be investigated before the generality of the mechanism can be established. With this in mind we are now extending the study to π-$C_3H_5Mn(CO)_4$ [10].

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10 Work in progress.