Final Comments

Important advances in the chemistry of dinitrogen complexes are found in the discovery of numerous transformations of coordinated N_2 into organonitrogen compounds through the carbon-nitrogen bond formation by reactions with organic compounds.

The reduction potentials of the alkylimide complexes reflect the electronic properties of the metal centres involved. Cathodic processes are observed when M^{IV} metal centres are present, and the strong electron-withdrawing capacity of the ligand facilitates the reduction on the metal.

Acknowledgments

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STUDY OF THE REDOX PROPERTIES OF SOME PALLADIUM AND NICKEL COMPLEXES WITH AZINE DIPHOSPHINE TYPE LIGANDS

M.F.N.N. Carvalho*[a], J. Čermák[b], F.A.Francisco[a], A.J.L. Pombeiro[a], S. Šabata[b]

[a]*Centro de Química Estrutural, Complexo 1, Instituto Superior Técnico, Av. Rovisco Pais,*
1096 Lisboa, codex, Portugal

[b]*Institute of Chemical Process Fundamentals, ASCR, Rozvojová 135, CZ-16502 Prague,*
Czech Republic

Abstract

The redox properties of $[\{L_2M\}_2(\mu\text{-}P^\frown P)_2]$ (M=Pd, L_2= $C(CO_2Me)\equiv C(CO_2Me)$ (1); M=Ni, L=CO (2) or Bu^tNC (3); $P^\frown P$= $PPh_2CH_2C(Bu^t)=NN=C(Bu^t)CH_2PPh_2$, $[Pd\{\eta^3\text{-}CH_2C(CH_3)=CH_2\}(P^\frown P)]Cl$ (4), $[PdCl\{PPh_2CH=C(Bu^t)NN=C(Bu^t)CH_2PPh_2\}]$ (5), or $[\{PdCl(\eta^1,\eta^2\text{-}CH_2C(CH_3)=CH_2)\}_2(\mu\text{-}P^\frown P)]$ (6), as well as $[Ni\{C(CO_2Me)\equiv C(CO_2Me\}(P^\frown P)]$ (7), were studied by cyclic voltammmetry and controlled potential electrolysis, in 0.2 M $[NBu_4][BF_4]$ /THF. By reductive electron transfer chemical reactivity was induced at complex (1) and the new species $[Pd(PPh_2CH_2C(Bu^t)=N\text{-}NC(Bu^t)=C(H)PPh_2)(MeCO_2C=C(H)CO_2Me)]$ was formed.

Key words

Redox properties, azine diphosphine , nickel, palladium, electrosynthesis.

Introduction

Since the first synthesis, in 1992 [1], of the azine diphosphine Z,Z-$PPh_2CH_2C(Bu^t)=N\text{-}N=C(Bu^t)CH_2PPh_2$, (Z,Z-$P^\frown P$), a considerable number of transition metal complexes with this ligand were prepared. Commonly, this versatile ligand isomerizes, upon coordination, to the E,Z form [2], affording mononuclear complexes. However, zero valent polynuclear palladium or platinum compounds were synthesized in which the ligand bridges two metal atoms keeping the Z,Z form [2].

In order to have an insight into the redox properties of the azine diphosphine and some of the derived palladium and nickel complexes we started their study by cyclic voltammetry and controlled potential electrolysis.

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Results and discussion

The redox behaviour of the following complexes was studied, in 0.2 M $[NBu_4][BF_4]$ / THF or CH_3CN, using a Pt wire working electrode: $[\{L_2M\}_2(\mu\text{-}P^\frown P)_2]$ (M=Pd, L_2=C(CO$_2$Me)≡C(CO$_2$Me) (1); M=Ni, L=CO (2) or Bu^{t}NC (3); $P^\frown P$= $PPh_2CH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PPh_2$, $[Pd\{\eta^3\text{-}CH_2C(CH_3)=CH_2\}(P^\frown P)]Cl$ (4), $[PdCl\{PPh_2CH=C(Bu^t)NN=C(Bu^t)CH_2PPh_2\}]$ (5), $[\{PdCl(\eta^1,\eta^2\text{-}CH_2C(CH_3)=CH_2)\}_2(\mu\text{-}P^\frown P)]$ (6), $[Ni\{C(CO_2Me)\equiv C(CO_2Me\}(P^\frown P)]$ (7), and that of the free azine diphosphine. The potentials are quoted *versus* saturated calomel electrode (SCE), using ferrocene ($[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ =0.54 V in THF or 0.40 V in CH_3CN) as internal standard.

For clarity the two families of transition metal complexes (with nickel or palladium metal sites) will be discussed separately and compared whenever relevant.

Nickel complexes

The dinuclear nickel complexes of general formula $[\{NiL_2\}_2(\mu\text{-}P^\frown P)_2]$ (L=CO (2) or CNBu^t (3)) [3] display by cyclic voltammetry an electrochemical behaviour dependent on the L ligand (Table 1).

Table 1 Cyclic voltammetry data[a] for the Pd and Ni azine diphosphine complexes

PALLADIUM COMPLEXES	$E^{red}_{1/2}$	NICKEL COMPLEXES	$E^{ox}_{1/2}$
1	-2.12[b]	2	0.86[c]
4	-2.37	3	-0.31[f]
5	-1.72[d,e]	7	-0.01

[a] Values in Volt ± 20 mV, *vs.* S.C.E., measured in THF at 200 mV/s, using $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ ($E^{ox}_{1/2}$=0.54V) as internal reference. [b] Loses reversibility at lower scan rates. [c] One irreversible wave, with half of the intensity is observed at E^{ox}_p=0.52 V. [d] Irreversible wave, E^{red}_p. [e] One oxidation wave, with *ca.* half of the intensity is observed at E^{ox}_p=0.52 V. [f] One ill defined anodic wave is detected at E^{ox}_p=0.71 V.

At the Ni-isocyanide complex one partially reversible oxidation wave ($E^{ox}_{1/2}$=-0.31 V) and a second very wide wave (E^{ox}_p=0.71 V) are observed. At the Ni-carbonyl complex one partially reversible wave ($E^{ox}_{1/2}$=0.86 V), preceded by a nearly half intensity irreversible one (E^{ox}_p=0.52 V), is detected. The possibility that the complexes undergo decomposition in solution is currently under study.

No original cathodic processes were detected for complexes (2) or (3).

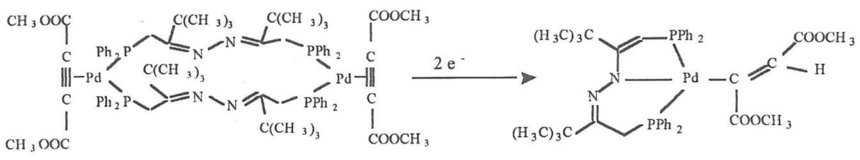
Controlled potential electrolysis performed on complex (3), at the potential of the lower potential oxidation wave, shows that two electrons *per* molecule are transferred, possibly one *per* each metal atom.

The related nickel zero monomer (7) also displays by cyclic voltammetry one anodic process, Table 1. It is unstable in THF solution, thus precluding further study by controlled potential electrolysis.

Palladium complexes

No original anodic process is detected at $[\{Pd(MeCO_2C\equiv CCO_2Me)\}_2(\mu\text{-}P^\frown P)_2]$ (1), in contrast with the behaviour observed at the Ni(0) analogues. However, a low potential cathodic process, with some reversible character (ν≥200 mV/s), is observed, which looses reversibility at lower scan rates. Upon reduction, on the reverse scan a new reversible oxidation wave is detected at $E^{ox}_{1/2}$=0.50 V.

Controlled potential electrolysis performed at the potential of the reduction process observed on complex (1) allowed to measure the transfer of two electrons *per* molecule. Work up of the electrolysed solution afforded orange crystals of a new compound which was characterized as $[Pd(PPh_2CH_2C(Bu^t)=N\text{-}N\text{-}C(Bu^t)=CHPPh_2)\{C(CO_2Me)=C(H)CO_2Me\}]$ [4]. At this process, reductive electron transfer to the palladium zero complex promoted alkyne to vinyl and azine to ene-hydrazone conversions. Moreover, in the overall process, the oxidation of Pd(0) to Pd(II) has occurred, reaction 1.



(1)

(1)

The possibility that the initial electron transfer process involved the azine moiety of the diphosphine ligand was not corroborated by the cyclic voltammetric study of the free azine diphosphine. In fact, no reductive process was detected and only one irreversible anodic wave was observed at E^{ox}_p=1.02 V (in CH_3CN). Moreover, the free alkyne ($MeCO_2C\equiv CCO_2Me$) displays one irreversible reduction process at E^{red}_p=-1.9 V, a value close to that measured for the complex, table 1.

The study of the redox properties of the new electrosynthesized species, $[Pd(PPh_2CH_2C(Bu^t)=N\text{-}N\text{-}C(Bu^t)=CHPPh_2)(CCO_2Me=CHCO_2Me)]$, shows that in addition to the anodic wave detected by cyclic voltammetry, a partially reversible reduction process occurs at $E^{red}_{1/2}$=-2.03 V.

The Pd(II) complex (4) displays also a partially reversible cathodic process, whereas complex (5), which is related to the above species formed upon reductive electron transfer to complex (1) in what concerns the hapticity of the phosphine ligand, displays one cathodic irreversible wave and one anodic reversible one at higher potentials by 0.31 and 0.21 V, respectively. Complex (6) is redox inactive, within the range of potential available in the experimental conditions used.

Final Comments

The redox properties of the zero valent complexes $[\{ML_2\}_2(\mu\text{-}\overset{\frown}{P\ P})_2]$ (M=Ni or Pd; $\overset{\frown}{P\ P}$= $PPh_2CH_2C(Bu^t)=N\text{-}N=C(Bu^t)CH_2PPh_2$) are dependent on their composition, in particular on the transition metal, e.g., no palladium oxidation was detected in contrast with nickel complexes.

The reductive electron transfer to the palladium dimer $[\{Pd(MeCO_2C{\equiv}CCO_2Me)\}_2(\mu\text{-}\overset{\frown}{P\ P})_2]$ induced chemical reactivity and alkyne to vinyl and azine to ene-hydrazone conversions occurred, in addition to palladium-phosphorus bond breaking, as well as Pd-P and Pd-N bond formation, affording $[\overline{Pd(PPh_2CH_2C(Bu^t)=N\text{-}N}\text{-}\overline{C(Bu^t)=C(H)P}Ph_2)(MeCO_2C=C(H)CO_2Me)]$.

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POTENTIOMETRIC STUDIES WITH BIOCOMPATIBLE POLYURETHANE- BASED MEMBRANES

Gomes, Ana M.R[≠]; Oliveira, Cristina M.R.R[*]; Rebelo, M.J.F[≠]; Camões, M.F.G.F.C. [≠]

[*] ***CECUL*** *- Centro de Electroquímica e Cinética da Universidade de Lisboa.*
[≠]*-Departamento de Química e Bioquímica da Faculdade de Ciências de Lisboa.*
Rua da Escola Politécnica Nº 58 1294 LISBOA CODEX

ABSTRACT

Polyurethane has been used lately as an alternative to PVC in the preparation of ISE membranes for clinical applications. This is due both to its biocompatibility [1] and to the claimed elimination of the protein asymmetry effect produced by serum at conventional PVC membranes [2].

Following previous work [3-7] electrodes have been prepared with TECOFLEX SG - 80A polyurethane and K^+ measurements have been performed in Bovine Serum Albumin (BSA) containing solutions.

Effects such as albumin concentration, sequence and age of solutions have been tested.

Simultaneous readings, in the same solution, have been taken with PVC based membranes and with polyurethane based ones *vs.* Saturated Calomel Electrode (SCE) and isotonic KCl electrodes (Ag/AgCl and Modified CE)

The results follow similar trends, without significant distinction being observed.

Therefore, the effects of protein on the potentiometric measurements, due to interaction with the membrane, if any, seem to be independent of the polymers tested.

These observations add evidence to the importance of the liquid-liquid junction potential contribution to the overall measurements.

Key Words - PVC, Polyurethane, membranes, K^+ selective electrode.

INTRODUCTION

Ion-selective electrodes are routinely used in clinical chemistry as well as in other applied fields despite the fact that some factors affecting the accuracy of measurements are still to be clarified [7].

This work follows previous studies [3-7] dealing with the influence of albumin and of reference electrode characteristics to the global cell potential. At this time we were interested in testing whether any difference is observed when the composition of the sensor membrane is modified from PVC to PU or not. In fact , this latter material has been lately used more as an alternative to PVC due to its characteristics concerning biocompatibility [1] and the elimination of the protein asymmetry effect produced by serum at conventional PVC membranes [2].

MATERIALS AND METHODS

KCl - Merck, P.A.; Valinomycin - Sigma V-0627; 2-Nitrophenyloctylether - Fluka, Selectophore; PVC - Fluka, pure; Polyurethane (PU) - "Tecoflex" SG-80A, Thermedics, Inc.; Potassium Tetrakys (4-chlorophenylborate) - Fluka, Selectophore; Tetrahydrophuran - Sigma T-5267; Bovine Serum Albumin (BSA) - Sigma A-3350

The solutions were prepared with conductivity water redistilled from distilled water, to which potassium permanganate and sodium hydroxide were added, under a current of nitrogen.