ANALYSIS OF COPPER(I) STABILITY IN THE CATIONIC $[Cu(CH_3CN)_{4-\mu}(Ph_3P)_{\mu}]^+$ SERIES OF COMPLEXES

ANA MARÍA LEIVA,* LEONARDO RIVERA and BÁRBARA LOEB*

Faculty of Chemistry, P. Catholic University of Chile, Casilla 6177, Santiago, Chile

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Abstract—NMR and electrochemical studies on the stability of copper(I) complexes of the type $[Cu(CH_3CN)_{4-n}(Ph_3P)_n]^+$ (n = 0-4) were carried out to explore the effect of phosphine ligands on stabilization. The effect of phosphine ligands was demonstrated by cyclic voltammetry and ³¹P NMR. A correlation between structural and electronic effects and the stability of the complexes was established.

Among the ligands known to stabilize copper(I), triphenylphosphine has been studied by several authors.^{1,2} Different coordination geometries have been observed for copper(I)–triphenylphosphine complexes, but the tetrahedral geometry is dominant.¹ Triphenylphosphine complexes are expected to be more stable than those of acetonitrile for copper(I),^{3,4} and CH₃CN should be displaced by PPh₃ in the equilibrium :

$$nPPh_{3} + [Cu(CH_{3}CN)_{4}]^{+} =$$

$$[Cu(CH_{3}CN)_{4-n}(Ph_{3}P)_{n}]^{+} + nCH_{3}CN. \quad (1)$$

Our work approaches the above problem by studying the electrochemical stability of the series of cationic complexes $[Cu(CH_3CN)_{4-n}(Ph_3P)_n]^+$ (n = 0-4). The related compound, $Cu(PPh_3)_3ClO_4$, was also studied and its behaviour compared to compounds of the above series.

EXPERIMENTAL

NMR spectra were obtained using a VARIAN XL 100 spectrometer with TMS and $H_3PO_4[85\%$ (external standard)] as references and CDCl₃ and CHCl₃ as solvents for ¹H and ³¹P, respectively.

The voltammometric measurements were carried out with a Wenking HP72 potentiostat, a Wenking VSG72 signal generator and a Graphtex WX2300 XY recorder. For coulometric measurements a Wenking EVI80 voltage integrator was used. All electrochemical measurements were performed under Argon, purified by a Hydrox Purifier, model 8301. The working electrode was a platinum disc for cyclic voltammetry measurements, and a platinum mesh for coulometry. The counter electrode was a platinum wire and the reference a Ag/AgCl (in aqueous tetramethyl ammonium chloride) electrode, adjusted to the SCE potential.⁵ All syntheses were carried out in dry solvents under nitrogen.

[Cu(CH₃CN)₃(PPh₃)]PF₆

PPh₃ (0.843 g, 3.21 mmol) was added to a solution of Cu(CH₃CN)₄PF₆⁶ (1.198 g, 3.21 mmol) in dichloromethane (100 cm³). The mixture was stirred at room temperature for 3 h and then concentrated to half its volume. The addition of diethyl ether (50 cm³) to this mixture precipitated a white solid, which was separated by filtration under nitrogen. This product was recrystallized from a 3:1 mixture of dichloromethane–ether. Yield: 85%; ¹H NMR (TMS, CDCl₃): 2.16 ppm (s, 9H; CH₃), 7.37 ppm (m, 15H; C₆H₅); ³¹P NMR (H₃PO₄ 85%, CHCl₃): 1.23 ppm (s).

[Cu(CH₃CN)(PPh₃)₃]ClO₄

This product was synthesized by following a modification of the method of White and coworkers,^{7b} with dichloromethane as the solvent; the solution was stirred over 3 h at room temperature.

^{*} Authors to whom correspondence should be addressed.

$Cu(PPh_3)_3ClO_4$

Recrystallization of $[Cu(CH_3CN)(PPh_3)_3]ClO_4$ from boiling methanol gave white crystals of the product. X-ray diffraction showed^{8a} the replacement of the coordinated acetonitrile by monodentate perchlorate, in agreement with literature reports.^{8b}

All other complexes were synthesized following literature procedures : $Cu(CH_3CN)_4PF_6$, $^6[Cu(CH_3CN)_2(PPh_3)_2]PF_6$ and $[Cu(PPh_3)_4]ClO_4$. ^{7a}

RESULTS AND DISCUSSION

(a) Nuclear magnetic resonance

The ³¹P NMR spectra of the copper(I) complexes (Table 1) show a shift of the phosphorus atom signal toward lower field as the number of phosphine ligands in the complex increases, implying a smaller shielding of this nucleus.¹⁰ This effect can be explained by a reduction in the π contribution to the Cu—P bond as the number of phosphine ligands increases. It is also corroborated by the Cu—P distances determined from X-ray structures of some copper complexes (Table 1),⁷ which show that larger Cu—P distances occur with an increasing number of phosphine ligands in the complex.

The transformation of the $[Cu(CH_3CN) (PPh_3)_3]ClO_4$ complex into the $Cu(PPh_3)_3ClO_4$ monodentate perchlorate is shown by the displacement of the ³¹P signal from 1.85 to 1.69 ppm, reflecting a shielding of the phosphorus nucleus due to a shortening of the Cu—P bond (from 233 to 231 ppm, as measured by X-ray diffraction⁸).

The ¹H NMR spectra of the complexes with acetonitrile ligands (Table 1) show a shift of the methyl group signal to higher field as the number of phosphine ligands in the complex increases, as expected for an increase in the electronic density around the methyl proton. This is corroborated by the X-ray data for complexes I, III and IV (Table 1) that indicate a lengthening of the Cu—N bond as the number of phosphine ligands increases.

(b) Electrochemical results

The voltammometric behaviour of triphenylphosphine has been extensively analysed and discussed;¹¹ in spite of some controversies,¹² it is now accepted that the phosphine undergoes an irreversible oxidation (at a potential > 1.0 V).¹³ This process is ascribed to the one-electron oxidation of triphenylphosphine to the PPh_3^{+} cationic radical.^{14,15} The oxidation is followed by a chemical reaction in which the radical, PPh₃⁺, reacts with nucleophilic components of the solution. In our system (DMF, TEAP 0.1 M, platinum disc working electrode) the oxidation of PPh₃ is observed at 1.38 V (vs SCE) and corresponds to a one-electron process (verified by coulometric measurements). voltammograms The cyclic for all the $[Cu(CH_3CN)_{4-n}(PPh_3)_n]^+$ (n = 0-4) compounds show an oxidation wave at potentials ranging from 0.6 to 0.92 V (Table 1), depending on the value of n. In addition, an oxidation process at the same potential (1.38 V) as free triphenylphosphine is observed for all the complexes (Fig. 1). The former wave is assigned to the oxidation of copper(I) to copper(II):

$$[\operatorname{Cu}(\operatorname{CH}_{3}\operatorname{CN})_{4-n}(\operatorname{PPh}_{3})_{n}]^{+} \longrightarrow$$
$$[\operatorname{Cu}(\operatorname{CH}_{3}\operatorname{CN})_{4-n}(\operatorname{PPh}_{3})_{n}]^{2+} + e. \quad (2)$$

	δ ³¹ P (ppm) ^a	δ^{1} H (ppm) ^{<i>a,b</i>}	$E_{\rm p}$ (vs SCE) ^c	d _{P—Cu} (pm)	d _{N—Cu} (pm)
$[Cu(CH_3CN)_4]^+ (I)$		2.14	0.6		199 ^d
$[Cu(CH_3CN)_3(PPh_3)]^+$ (II)	1.27	2.16	0.6	_	
$[Cu(CH_{3}CN)_{2}(PPh_{3})_{2}]^{+}$ (III)	1.72	2.11	0.82	226 ^e	200°
$[Cu(CH_3CN)(PPh_3)_3]^+$ (IV)	1.85	1.96	0.85	233e	210 ^e
$[Cu(PPh_{3})_{4}]^{+}(V)$	2.716		0.92	252.4-260.5	

Table 1. NMR chemical shifts, oxidation potentials and M—L distances for the $[Cu(CH_3CN)_{4-n}(PPh_3)_n]^+$ (n = 0-4) series of complexes

^{*a*} δ ³¹P ref. H₃PO₄ 85% (45, MHz); δ ¹H TMS (100 MHz); solvent CDCl₃.

^b Methyl (CH₃CN) proton.

^c ± 20 mV; DMF (TEAP 0.1 M); under the same conditions E^{0} (ferrocene/ferricinium) = 0.4 V.

^{*d*} Reference 7(c).

^e Reference 7(b).

^fReference 7(a).



Fig. 1. Cyclic voltammetry for the $[Cu(CH_3CN)(PPh_3)_3]$ ClO₄ complex ($v = 200 \text{ mV s}^{-1}$) in DMF (TEAP 0.1 M) using a platinum disc as working electrode.

Controlled potential electrolysis corresponding to this oxidation generates, after the passage of one electron, a green coloured compound, probably a copper(II) complex. The current intensity does not manifestly decrease during the process, even after the passage of more than three electrons. The green colour quickly dissappears when the electrolysis is stopped. This behaviour suggests that the oxidation is complicated by a subsequent chemical reaction, probably the reduction of copper(II) by triphenylphosphine released during the electrochemical oxidation of the copper(I) complex [triphenylphosphine has a low affinity for copper(II)]. The ability of triphenylphosphine to reduce copper(II) is well known.⁶ However, in this case, the subsequent chemical reduction is rather slow compared to the electrochemical oxidation, and therefore the copper(II) compound can be detected during the electrolysis. Similar behaviour has been shown for a series of rhenium(I) complexes of the type $[Re(CO)_2(PPh_3)_2\{(ArN)_2X\}]$ (X = N, CH; Ar = benzyl and substituted benzyl),¹³ where the existence of subsequent chemical reactions was proven by several electrochemical criteria.

In the cyclic voltammetry of $Cu(PPh_3)_3ClO_4(VI)$ the oxidation wave appears at 0.6 V, i.e. at a considerably lower potential than the corresponding wave of $[Cu(CH_3CN)(PPh_3)_3]ClO_4$ (Table 1). Since the oxidation process for the related complex, $Cu(PPh_3)_3Cl$ (VII),¹⁶ is also observed at 0.6 V, we conclude that VI and VII generate the same species in solution. An explanation for this behaviour could be the substitution of the solvent (DMF) for the perchlorate or chloride anion. The greater ease of oxidation of the solvated species reflects the greater affinity of DMF for copper(II).¹⁷

The electrochemical reduction of the complexes in the series was also investigated. A cathodic wave is observed for all of the complexes, the shape of it suggesting a metal deposit on the electrode. Indeed, controlled potential electrolysis for this process generated a copper deposit on the working electrode, after the passage of one electron. The voltammogram of the remaining solution corresponds to free triphenylphosphine, as would be expected for a $Cu^1 \rightarrow Cu^0$ reduction.

CONCLUSIONS

The increase in the Cu—P and Cu—N bond lengths with the number of phosphine ligands in the $[Cu(CH_3CN)_{4-n}(PPh_3)_n]ClO_4$ (n = 0-4) complexes (Table 1) could be indicative of a corresponding decrease in stability. However, the greater crystal symmetry observed for the complexes with high values of *n* would suggest the opposite.* The actual stability tendency is clearly manifested by cyclic voltammetry, where the anodic wave related to the Cu¹/Cu^{II} oxidation moves to more positive potentials as the number of phosphine ligands in the complex increases.

In addition to the crystal symmetry effect, the enhanced stability can be ascribed to the $M \rightarrow L$ back-donation effect.⁴ Since Cu¹- d^{10} is an electronrich metal it can be regarded as a good π donor to phosphorus, which acts as a π base via its empty d orbitals. The electron density displacement is not possible with acetonitrile as the ligand since there are no energetically appropriate $d\pi$ orbitals on the nitrogen atom for this type of bond.

A comparison between the structure of the $Cu(PPh_3)_3ClO_4$ complex and that of $[Cu(CH_3CN)(PPh_3)_3]ClO_4$ reveals that the former belongs to a trigonal system,⁸ while the latter belongs to an orthorhombic one.^{7b} Therefore, the cyclic voltammetries should reflect the greater stability of $Cu(PPh_3)_3ClO_4$, but since the species in solution are different [due to the solvation of $Cu(PPh_3)_3ClO_4$] the oxidation of the latter complex is easier, given the greater affinity of DMF for copper(II).

It is concluded that, in this series of copper(I) complexes, a greater ordering of the structure increases the stability only if the species is not altered in solution, as seems to be the case for the $[Cu(CH_3CN)_{4-n}(PPh_3)_n]^+$ (n = 0-4) series of com-

^{*} The $[Cu(CH_3CN)_2(PPh_3)_2]ClO_4$ complex belongs to a monoclinic system with marked distortion of the coordination polyhedra (P—Cu—P and N—Cu—N angles of 127.6 and 99.2°, respectively⁷), while the system for Cu(PPh_3)_4ClO_4 is rhombohedral with P—Cu—P angles of 109.6 and 109.3°.^{7a}

plexes. On the other hand, the electronic effect on stability is reflected in the chemical shifts observed in the NMR spectra, as well as in the displacement of the electrochemical oxidation wave.

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