Inorganica Chimica Acta, *157* (1989) 51–56

The Direct Electrochemical Synthesis of Metal Complexes of 2,2′-Dipyridylamine

RAJESH KUMAR and DENNIS G. TUCK
Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont. N9B 3P4, Canada

(Received July 15, 1988)

Abstract

The electrochemical oxidation of a metal anode in a non-aqueous solution of dpaH (dpaH = 2,2′-dipyridylamine) under nitrogen gives M(dpa)$_n$ complexes in high yield (M = Cu, Ag, Tl, $n = 1$; M = Zn, Cd, $n = 2$). In the presence of O_2, copper yields Cu(dpa)$_2$. When the oxidations were repeated in the presence of neutral ligands, adducts were only obtained for Cu^I with phosphine donors. Both Cu(dpa) and Cu(dpa)$_2$ react with CS_2 to give dithiocarbamate complexes, as do the Ph_3P and dppe adducts of Cu(dpa) (dppe = 1,2-bis(diphenylphosphino)ethane). The thallium(I) compound undergoes ligand exchange with C_6H_5OH, C_6H_5SH or $C_5H_{11}SH$ to give TlOR or TlSR.

Introduction

Recent papers from this laboratory have described the use of direct electrochemical synthesis for the preparation of thiolato [1–5], diphenylphosphido [6], carboxylato [7] and catecholato [8,9] derivatives of main group and transition metals. The essence of the method is the oxidation of a sacrificial metal anode by the appropriate anion which is generated electrochemically, and the overall result is the one-step synthesis of salts of very weak acids, which in general do not react directly with such metals under thermal conditions. An earlier attempt [10] to use this technique for the synthesis of $M(NR_2)_2$ compounds was not successful, apparently because of a competing reaction between NR_2^- and solvent (acetonitrile), but we now report that the use of the substituted amine 2,2′-dipyridylamine (dpaH) allows the synthesis of a number of M(dpa)$_n$ compounds in high yield. A simple change in solution conditions allows the preparation of certain adducts with phosphorus donor ligands. The insertion reaction of carbon disulphide with some copper(I) compounds has been investigated, as has the use of the thallium(I) salt as a ligand transfer reagent.

Experimental

Materials

Metal rods (copper, silver, gold, zinc, cadmium, indium, thallium) (Alfa) were first treated with conc. nitric acid for a few minutes to remove any surface film, and then washed repeatedly with distilled water, after which the dried metal was lightly abraded with fine sandpaper and polished with tissue. Acetonitrile was distilled from calcium hydride and stored over molecular sieves. Carbon disulphide was distilled from phosphorus pentoxide. All other reagents were used as supplied.

Analysis and Spectroscopy

All metals except silver were determined by atomic absorption spectrophotometry, using an IL-251 instrument; silver was determined gravimetrically. Microanalysis was by Guelph Chemical Laboratories Ltd.

Infrared spectra were recorded on a Nicolet 5DX instrument as KBr discs; ^{1}H nuclear magnetic resonance spectra were run on a Perkin-Elmer EM360 spectrometer and ^{31}P spectra with a Bruker CXP instrument.

Electrochemical Procedures

The electrochemical procedure followed that described in earlier papers [1–9]. The anode, in the form of a rod, 3 mm diameter, was suspended via platinum wire in the solution in a 100-ml tall-form beaker. The cathode was a coiled platinum wire, and the cell was of the general form $M_{(+)}/CH_3CN + dpaH(+ligand)/Pt_{(-)}$. Dry nitrogen gas was bubbled gently through the solution phase during the electrolysis to exclude oxygen, and this procedure also ensured that the contents of the cell were constantly agitated. The details of cell composition, electrical conditions, and electrochemical efficiency E_F (defined as moles of metal dissolved per Faraday of charge) are given in Table 1. Chemical yields were generally better than 90%, calculated on the basis of the quantity of metal dissolved from the anode.

0020-1693/89/$3.50

TABLE 1. Experimental Conditions for the Electrochemical Synthesis of Derivatives of 2,2'-dipyridylamine (= HL)

Metal anode	Mass HL (g)[a]	Ligand, mass (g)[b]	Initial voltage (V)	Initial current (mA)	Time of electrolysis (h)	Mass of metal dissolved (mg)	E_F (mol F^{-1})	Product
Cu	0.56		20	30	1.0	79	1.11	CuL
Cu	0.33	Et_3N, 0.7	30	30	1.0	72	1.01	CuL
Cu	0.25	tmen, 0.8	25	30	1.4	86	0.96	CuL
Cu	1.03	bpy, 0.5	10	30	1.0	78	1.09	CuL
Cu	1.03	phen, 0.5	10	10	4.0	95	1.00	CuL
Cu	0.69	Ph_3P, 1.8	10	30	3.0	226	1.06	CuL·$2Ph_3P$
Cu	0.48	dppm, 1.6	25	40	2.0	203	1.07	CuL·0.5dppm
Cu	0.56[c]	dppe, 1.0	30	30	1.0	76	1.07	CuL·1.5dppe
Cu	0.51	O_2	25	30	1.0	76	1.07	CuL_2
Ag	0.57		30	30	0.57	72	1.05	AgL
Au	0.71		30	30	0.67	4		see text
Zn	0.74		30	30	3.4	118	0.50	ZnL_2
Zn	1.00	tmen, 0.8	25	40	3.0	145	0.50	ZnL_2
Zn	1.00	py, 2.0	30	40	3.0	146	0.50	ZnL_2
Cd	0.80		25	30	1.4	95	0.53	CdL_2
Cd	0.57	py, 2.0	15	30	1.3	94	0.51	CdL_2
In	1.00		20	25	2.0	236	1.10	see text
Tl	1.00		30	40	0.83	255	1.00	TlL

[a] Dissolved in 60 ml CH_3CN containing *ca.* 25 mg Et_4NClO_4. [b] tmen = *N,N,N',N'*-tetramethylethanediamine; bpy = 2,2'-bipyridyl; phen = 1,10-phenanthroline; dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; py = pyridine. [c] In 40 ml CH_3CN + 20 ml benzene + *ca.* 25 mg Et_4NClO_4.

TABLE 2. Analytical and Spectroscopic Results for Derivatives of 2,2'-dipyridylamine (= HL)

Compound[a]	Colour	M (%)		^1H NMR[b]	Solvent	^{31}P NMR[c] (in CH_2Cl_2)
		found	calc.			
HL	colourless			9.73(s) (1H); 8.17–6.50(m)	$CDCl_3$	
CuL	yellow	26.9	27.2	insoluble		
CuL·$2PPh_3$	yellow	8.31	8.39	8.5–7.5(m); see text	CD_2Cl_2	−2.14 (−5.49)
CuL·0.5dppm	yellow	14.0[d]	14.9	7.7–6.6(m); 2.07(t); see text	CD_2Cl_2	−13.2 (−22.9)
CuL·1.5dppe	yellow	7.46[e]	7.65	8.5–7.3(m) (38H); 2.48(s) (6H)	CD_2Cl_2	−11.2 (−12.5)
CuL_2	green	16.5[f]	15.7	paramagnetic		
CuL·CS_2	orange	19.8	20.5	insoluble		
CuL_2·$2CS_2$	red–black	10.8	11.4	paramagnetic		
CuL·$2Ph_3P$·CS_2	yellow	7.31[g]	7.62	8.48–7.28(m)	CS_2	−0.37[h] (−5.49)
CuL·dppe·CS_2	orange	9.16	8.97	8.40–7.18(m) (28H); 2.34(q) (4H)	CD_2Cl_2	−6.76, −8.55 (−12.5); see text
AgL	colourless	37.8	38.8	8.4–6.4(m)	CF_3COOH	
ZnL_2	colourless	15.2	16.1	8.3–6.4(m)	d_6-dmso	
CdL_2	off-white	26.2	24.8	7.3–6.6(m)	CS_2	
TlL	off-white	53.9	54.6	8.5–6.4(m)	CF_3COOH	

[a] Abbreviations as in Table 1. [b] Chemical shifts, ppm from Me_4Si; relative integrated intensities in parentheses. [c] Chemical shifts, ppm from external 85% H_3PO_4; values in parentheses for free ligand. [d] Found: C, 63.4; H, 4.74; N, 10.2. Calc.: C, 63.4; H, 4.46; N, 9.87%. [e] Found: C, 71.5; H, 5.59; N, 5.47. Calc.: C, 70.8; H, 5.30; N, 5.06%. [f] Found: C, 60.0; H, 4.17; N, 21.1. Calc.: C, 59.5; H, 3.96; N, 20.8%. [g] Found: C, 69.0; H, 4.92; N, 4.90. Calc.: C, 67.7; H, 4.56; N, 5.04%. [h] In benzene solution.

The products of these, and other reactions discussed below, were characterized by analysis, ^1H and ^{31}P NMR spectroscopy (Table 2) and infrared spectroscopy. Apart from the general features of the spectra of dpaH and its derivatives, the most useful diagnostic feature is the ν(C–N) vibration which occurs at 1436 cm^{-1} in the parent amine but is replaced by two strong bands in the 1420–1475 cm^{-1} range in the metal complexes. The ^{31}P NMR spectra are discussed below; the ^1H spectra confirm the presence of coordinated dpa and of the neutral donor ligands.

Details of the synthesis and isolation of the compounds of the elements investigated are given below.

Copper(I) Derivatives

The electrochemical oxidation of copper to give 2,2′-dipyridylamido copper(I) occurred smoothly, with the product depositing in the cell as electrolysis proceeded. This material was collected, washed with acetonitrile and then diethyl ether (or petroleum ether) and dried *in vacuo*. The compound is an amorphous powder, insoluble in all common organic solvents.

The addition of bpy, phen, tmen or Et_3N to the solution phase before electrolysis caused no change in the nature of the product, but with the phosphorus donors Ph_3P, dppm or dppe, the reaction followed a different pathway. The solution became deep yellow in colour as the electrolysis proceeded; subsequent removal of solvent by bubbling nitrogen through the solution, or slow cooling of the mixture, produced yellow crystals which were collected, washed with cold acetonitrile, and dried in a stream of nitrogen. The resultant adducts (see Table 1) are sparingly soluble in benzene or acetonitrile, but dissolve in carbon disulphide (see below).

Bis(2,2′-dipyridylamido)copper(II)

Oxygen gas was bubbled through the solution before and during the electrolysis. A green microcrystalline product, subsequently identified as CuL_2, precipitated as the oxidation proceeded, and was collected, washed with acetonitrile and then n-pentane and dried *in vacuo*. The compound is soluble in methanol, ethanol, tetrahydrofuran, dimethylsulphoxide, *N,N*-dimethylformamide, dichloromethane and carbon disulphide.

Silver and Gold

The electrochemical oxidation of silver to give the insoluble AgL compound followed the same course as that of copper. With gold, only *ca.* 4 mg of metal dissolved during 1 h, and we conclude that the electrochemical method is not suitable for the synthesis of gold derivatives of dpa. Similar results were found in attempts to prepare gold thiolates by the electrochemical oxidation of the metal with solutions of RSH (R = n-Cu_4H_9, C_6H_5) [4].

Zinc and Cadmium

The oxidation of zinc produced a white solid which deposited in the bottom of the cell, and was collected, washed (CH_3CN, n-pentane) and dried *in vacuo*. A black coating on the anode surface did not apparently affect the reaction.

With cadmium, a yellow–white solid deposited during the electrolysis, but we also observed the formation of a black deposit on the cathode after *ca.* 30 min. This continued to grow, and care was taken to stop the electrolysis before this solid flaked off the cathode and contaminated the product. We did not attempt to identify this black cathodic deposit.

Attempts to prepare adducts of ZnL_2 or CdL_2 by adding either pyridine or tmen to the electrolyte phase were unsuccessful, with only the ML_2 species being obtained.

Indium and Thallium

In the case of indium, a red coloration developed around the anode as the electrolysis proceeded; this color dissipated as the species concerned moved away from the anode. As the electrolysis continued, the solution became cloudy, but no precipitate formed; a large quantity of indium accumulated around the cathode. We were unable to recover any indium compound from the solution phase.

With thallium, a cream–white solid began to deposit within *ca.* 10 min of the beginning of the electrolysis. At the same time, a black adherent deposit formed on the cathode. The precipitate was collected, washed with cold acetonitrile and dried *in vacuo.*

Reactions of Copper Derivatives with Carbon Disulphide

(i) Cu^I(dpa) (0.5 g, 2.14 mmol) was suspended in carbon disulphide (50 ml) and the mixture stirred for 3 d at room temperature. After this period, during which the initially yellow solid became orange, the product was collected, washed with n-pentane and dried *in vacuo*; yield of Cu(dpa)·CS_2, 0.66 g, 95%.

(ii) $Cu^{II}(dpa)_2$ (0.5 g, 1.24 mmol) dissolved readily in carbon disulphide (100 ml) at room temperature to give a dark red solution. This solution was stirred for *ca.* 2 h, at which point a red–black solid began to precipitate. After 3 d further stirring, the resultant solid was collected, washed with n-pentane and dried *in vacuo*; yield of $Cu(dpa)_2 \cdot 2CS_2$, 0.65 g, 95%.

(iii) Addition of Cu(dpa)·$2PPh_3$ (0.96 g, 1.27 mmol) to carbon disulphide (100 ml) gave a clear red–orange solution. This solution was stirred for

16 h, after which traces of solid were removed and the volume of the filtrate slowly reduced *in vacuo*. The resultant yellow powder was washed and dried *in vacuo*; yield of $Cu(dpa)\cdot 2PPh_3\cdot CS_2$, 0.64 g, 60%.

(iv) A similar reaction with $Cu(dpa)\cdot 1.5dppe$ (0.46 g, 0.55 mmol) and carbon disulphide (100 ml) yielded a red–brown solution, which during 24 h stirring threw down an orange–brown solid, which was collected, washed and dried as in (iii); yield of $Cu(dpa)\cdot dppe\cdot CS_2$, 0.19 g, 50%.

Ligand Transfer Reactions with Tl(dpa)

Since dpaH is a weak acid, the ligand exchange reaction $Tl(dpa) + RH \rightarrow TlR + dpaH$ was briefly investigated for R = PhO, PhS and $C_5H_{11}S$. In each case a suspension of Tl(dpa) (0.20 g, 0.53 mmol) in acetonitrile (30 ml) was treated with RH, and the mixture stirred for 4 h. The resultant solid was collected, washed with cold acetonitrile (2 × 5 ml) and dried *in vacuo*. The filtrate was slowly evaporated to give a solid identified by melting point (m.p.) (95 °C) and ^1H NMR spectroscopy as dpaH. Specific details are as follows:

(i) Tl(dpa) and C_6H_5OH (0.06 g, 0.64 mmol); off-white solid product, m.p. 233 °C (lit. value [11] for $TlOC_6H_5$ 231 °C). Found: Tl, 67.9; calc.: Tl, 68.7%.

(ii) Tl(dpa) and C_6H_5SH (0.3 ml, 0.32 g, 2.9 mmol); yellow solid product, m.p. 255 °C (lit. value [12] for $TlSC_6H_5$ 258 °C). Found: Tl, 65.9; calc.: Tl, 65.2%.

(iii) Tl(dpa) and $CH_3CH_2C(CH_3)_2SH$ (0.5 ml, 0.42 g, 4.0 mmol); yellow solid product, m.p. 170–175 °C. Found: Tl, 67.1%; calc. for $TlSC_5H_{11}$: Tl, 66.4%. This compound does not appear to have been reported previously.

Since the compounds $TlOC_6H_5$, $TlSC_6H_5$ and $TlSC_5H_{11}$ are insoluble in most common solvents, the characterization depended on metal analysis, m.p., and infrared spectroscopy. In each case, the IR spectrum differed from that of the parent RH compound only in the absence of the ν(O–H) or ν(S–H) mode.

Results and Discussion

Preparative and Electrochemical

The preparation of $M(dpa)_n$ complexes of a variety of late transition and main group metals is readily achieved by the electrochemical methods described above. This efficient one-step route to these compounds gives the products in high yield and purity, and although we chose to work on a relatively small scale, there is no difficulty in using larger cells or using cells in series. The products are those of the elements in their conventional oxidation states. We return to the preparation of adducts of $M(dpa)_n$ species below.

The significance of the electrochemical efficiency, defined as moles of metal dissolved from the anode per Faraday of charge, has been emphasized previously. In the present work, we find that $E_F = 1.05 \pm 0.03$ mol F^{-1} for copper, silver and thallium, implying the sequence

$$\text{cathode: } dpaH + e \longrightarrow \tfrac{1}{2}H_2(g) + dpa^- \qquad (1)$$

$$\text{anode: } dpa^- + M \longrightarrow M(dpa) + e \qquad (2)$$

This sequence holds even when the product is $Cu(dpa)_2$ as is the case when oxygen is present in the cell, showing that the formation of this copper(II) product is the result of oxidation after the anodic reaction. The simplest reaction in this latter case is

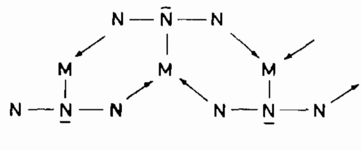
$$2Cu(dpa) + 2dpaH + \tfrac{1}{2}O_2 \longrightarrow 2Cu(dpa)_2 + H_2O \qquad (3)$$

The formation of adducts by CuL under these electrochemical conditions occurs only with phosphorus donors, but the E_F value remains at essentially 1.0 mol F^{-1}, showing that the ligation by these donors is, not unexpectedly, a process which takes place after the anodic oxidation. Similar conclusions have been reached in previous syntheses of adducts of the primary products.

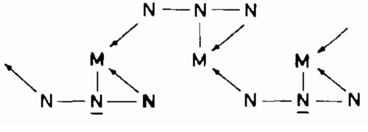
For zinc and cadmium, $E_F = 0.51 \pm 0.1$ mol F^{-1}, establishing a sequence of reactions similar to eqns. (1) and (2), but involving the attack of two L^{-1} anions on the metal.

Although no stable derivative of indium could be isolated, an anodic reaction such as eqn. (2) obviously occurs in the cell, and the E_F value implies that the primary product is the indium(I) derivative In(dpa). A number of indium(I) derivatives of anionic oxygen or sulphur donor ligands have been prepared electrochemically [13], but no stable analogues with nitrogen ligands are known at the present time [14].

The products are all insoluble in the electrolytic medium used (see Table 1), and resist interaction with other nitrogen ligands under the conditions used. These facts are no doubt related, and can be understood in terms of a homopolymeric structure in which the nitrogen atoms of the pendant pyridyl groups serve to coordinate internally and to cross-link, as the following simplified diagram shows (N-N̄-N = 2,2′-dipyridylamine anion).



or



The extent to which one of these modes dominates must clearly depend on the size and optimum coordination number of the metal ion concerned. Given this favoured internal coordination, it is clear that external (*i.e.* added) ligands will not in general compete favourably for metal coordination, and are therefore not incorporated into the M(dpa)$_n$ homopolymer. The exceptions to this involve the mono- or bidentate phosphorus donors Ph_3P, dppm and dppe. Here the stoichiometry of the product depends on the particular ligand, and it is significant that the products are soluble in the reaction mixture and are brought out of solution only by removal of solvent. It seems very probable that these Cu(dpa)P_n species are in fact oligomeric cage structures in the solid state, but given the wide variety of such structures known for copper(I)–thiolato complexes [15], any speculation about their nature would be premature. The ^{31}P chemical shifts of dppm and dppe, relative to the free ligands, show that these ligands are coordinating in a bridging mode [16–18], which is again in keeping with the proposed cage structures (*cf.* ref. 19).

Reaction of Cu(dpa)$_n$ with Carbon Disulphide

The uncomplexed copper(I) and copper(II) compounds, and the copper(I) adducts with Ph_3P or dppe, all react readily with carbon disulphide at room temperature. The reaction of carbon disulphide with secondary amines to give the corresponding dithiocarbamate anion, leading to metallic complexes of this latter type of ligand, is well established [20], but examples of the *in situ* insertion of CS_2 into an existing $M{-}NR_2$ bond are still few in number.

The detailed structures of the products must be in doubt, for reasons similar to those noted above for the parent Cu(dpa) adducts, but in each case, the analytical results indicate the insertion of CS_2 into a Cu–N bond. The copper(I) species was prepared from the insoluble Cu(dpa), and the product Cu(dpa)CS_2 is similarly insoluble, suggesting that cross-linking plays a dominant role in producing a homopolymer in both cases. In contrast, Cu(dpa)$_2$ dissolves in CS_2, but the Cu(dpa)$_2$·2CS_2 species eventually precipitates from the reaction mixture; a slow oligomerization process in solution to produce an insoluble cage would explain this behaviour. The phosphine adducts Cu(dpa)·2PPh_3 and Cu(dpa)·1.5dppe dissolve in CS_2, and again in the latter case the product is thrown out of solution spontaneously, and here the insertion product has a different stoichiometry, Cu(dpa)dppe·CS_2, from that of the starting material in terms of the Cu:dppe ratio. The identification of these structures must await planned X-ray crystallographic studies.

The NMR spectra are not very helpful in the case of Cu(dpa)·CS_2, since it is insoluble, and the comparison of Cu(dpa)·2Ph_3P and Cu(dpa)·2Ph_3P·CS_2 shows a small but similar shift in ^{31}P resonance from that of Ph_3P itself (Table 2) indicating coordination to the metal. For Cu(dpa)·dppe·CS_2 and its parent Cu(dpa)·1.5dppe (and Cu(dpa)·0.5dppm), the ^{31}P shifts are consistent with the presence of bridging diphosphino ligands. The solution of Cu(dpa)·dppe·CS_2 in CD_2Cl_2 underwent significant change within the time required for recording the spectrum, as evidenced by the precipitation of an unidentified green product.

The infrared spectra of each of these compounds showed characteristic ν(C–S) and ν(C–N) modes at *ca.* 1000 and 1400 cm^{-1} respectively. We therefore conclude that CS_2 indeed inserts into the Cu–N bond of Cu(dpa), specifically at the amido rather than pyridyl nitrogen atom, although these latter donor sites may still play an important structural role, despite the Cu---N distances involved.

Acknowledgement

This work was supported in part by Operating Grants (to DGT) from the Natural Sciences and Engineering Research Council of Canada.

References

1 F. F. Said and D. G. Tuck, *Inorg. Chim. Acta, 59* (1982) 1.
2 J. L. Hencher, M. A. Khan, F. F. Said, R. Sieler and D. G. Tuck, *Inorg. Chem., 21* (1982) 2787.
3 J. L. Hencher, M. A. Khan, F. F. Said and D. G. Tuck, *Polyhedron, 4* (1985) 1263.
4 R. K. Chadha, R. Kumar and D. G. Tuck, *Can. J. Chem., 65* (1987) 1336.
5 H. E. Mabrouk and D. G. Tuck, *Inorg. Chim. Acta, 145* (1988) 237.
6 T. A. Annan, R. Kumar and D. G. Tuck, *J. Chem. Soc., Chem. Commun.*, (1988) 446.
7 N. Kumar, D. G. Tuck and K. D. Watson, *Can. J. Chem., 65* (1987) 740.
8 H. E. Mabrouk, D. G. Tuck and M. A. Khan, *Inorg. Chim. Acta, 129* (1987) 75.
9 H. E. Mabrouk and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, (1988) 2539.
10 A. Osman and D. G. Tuck, unpublished results.
11 L. P. McHatton and M. J. Soulal, *J. Chem. Soc.*, (1952) 2771.
12 H. Gilman and R. K. Abbott, *J. Am. Chem. Soc., 71* (1949) 659.
13 R. Kumar, H. E. Mabrouk and D. G. Tuck, unpublished results.
14 D. G. Tuck, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds.), *Comprehensive Coordination Chemistry*, Vol. 3, Pergamon, Oxford, 1987, p. 153.
15 (a) I. G. Dance, *Polyhedron, 5* (1986) 1037; (b) P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev., 76* (1987) 121.
16 G. K. Anderson, H. C. Clark and J. A. Davies, *J. Organometal. Chem., 210* (1981) 135.

17 S. J. Cooper, M. P. Brown and R. J. Puddephatt, *Inorg. Chem., 20* (1981) 1374.
18 A. R. Sanger, *J. Chem. Soc., Dalton Trans.,* (1981) 228.
19 M. A. Khan, R. Kumar and D. G. Tuck, *Polyhedron, 7* (1988) 49.
20 D. Coucouvanis, *Prog. Inorg. Chem., 11* (1970) 233; *22* (1979) 301.