X=Y–ZH Systems as Potential 1,3-Dipoles. Part 6. Metallo-1,3-dipoles. Cycloadditions of Divalent Metal Complexes of Glycine and Alanine Imines to Electronegative Olefins

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Copper(II), zinc(II), and cadmium(II) complexes of imines derived from α-oxo acids and glycine or alanine undergo stereospecific cycloaddition at room temperature to 1,2-disubstituted electronegative olefins in the presence of weak base. Corresponding reactions of lead(II) complexes give insoluble cycloadducts. In contrast, the reactions of the same metallo imines with methyl acrylate, phenyl vinyl sulphone, and acrylonitrile frequently give mixtures of regio- and stereo-isomers. These mixtures are shown to arise by stereoisomerisation of initial cycloadducts formed by a $4\pi + 2\pi$ concerted cycloaddition of intermediate metallo-1,3-dipoles.

We have recently described three novel methods for the generation of 1,3- or 1,5-dipoles involving prototropy. Thus dipoles are generated by prototropy of X=Y–ZH systems (1) $\rightleftharpoons$ (2),[1] by decarboxylative transamination (3)→(4),[2] and by a 1,5-H shift (5)→(6)→(7) in imminium ions generated from primary and secondary amines.[3] We have recently characterised a stable example of an azomethine ylide (2; X=Z=C, Y=N) by X-ray crystallography.[4] The dipoles (2), (4), and (7) can be trapped both inter-[3,5] and intra-[6]molecularly by alkenes or alkynes to give a wide range of 5-membered heterocycles. In the general system (1) $\rightleftharpoons$ (2) either X, Y, Z or H could conceptually be replaced by a metal ion. Thus, replacement of H by M would lead to the potentially metallotropic system (8) $\rightleftharpoons$ (9). The present paper is concerned with replacement of H in (2) by a divalent metal ion leading to (9). Such systems were suggested by us in an earlier paper[7] and examples where (9) may be formed catalytically were presented subsequently.[8]

A family of metallo-1,3-dipoles (9) can be visualized in which the overall molecular charge will vary with the valency of the metal ion M and the number of associated counterions. Thus (9)
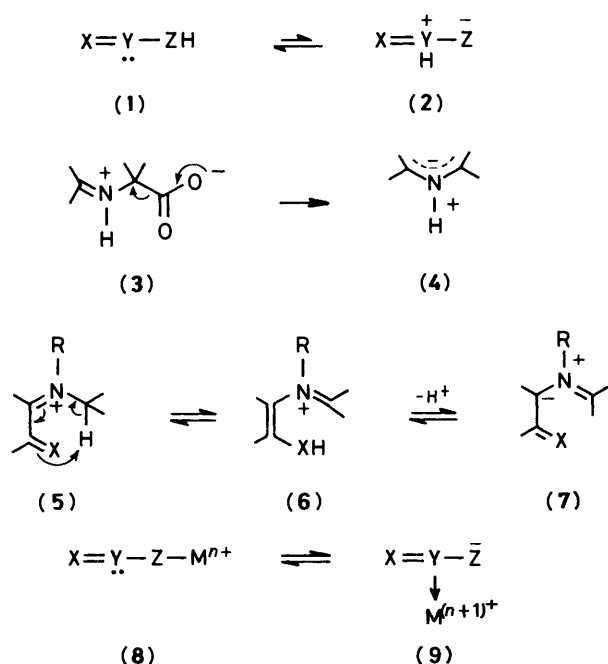
could be neutral, cationic, or anionic and the general term metallo-1,3-dipoles is used to emphasise the underlying relationships of these species.
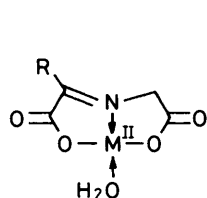
A recent publication by Casella *et al.*,[9] on the reaction of *N*-(1-carboxyethylidene)glycinatocopper(II) with several activated olefins to give pyrrolidines prompts us to publish our observations and conclusions on these and related reactions which differ in important respects from those of Casella *et al.*

Amino acids readily form imines with carbonyl compounds. When the carbonyl compounds possess additional groups capable of co-ordinating to metal ions these imines form stable, isolable, metal complexes. Thus, metal complexes of imines of α-amino acids and salicylaldehyde,[10] pyridoxal,[11] pyruvic acid[12] and 3-hydroxymethylenebornan-2-one[13] are known. Co-ordination of amino acids and peptides to metal ions results in the activation of their α-methylene or α-methine protons. This activation is enhanced in metal complexes of imines of amino acids and peptides,[14] *e.g.* the copper complex (10a) derived from pyruvic acid and glycine condenses regiospecifically with aldehydes under weakly basic conditions to give β-hydroxy amino acids (11).[15] Analogous regiospecific reactions of intermediates similar to (12) are reported to occur with alkyl halides[14] and Michael acceptors.[16]

The intermediate (12) in the conversion (10a)→(11) is a member of the class of metallo-1,3-dipoles (9) with an overall anionic charge. We have been studying the $4\pi + 2\pi$ cycloadditions of such species using the imine metal complexes (10a—f), (13), and (14). The methylene or methine protons in (10) and (13) are sufficiently reactive to be removed by triethylamine at room temperature. Thus, cycloadditions were conducted at room temperature for 4.5—12 h in pyridine containing 1 mol equivalent of triethylamine when 1,2-disubstituted electronegative olefins were used as trapping agents. These conditions are essentially the same as those used by Casella *et al.* except for a substantially shorter reaction time. Cycloadditions occur in pyridine alone in some cases but are slower. Thus (10a) reacts with maleimide in pyridine containing 1 mol equivalent of triethylamine over 8 h to afford a cycloadduct copper complex. Removal of the copper by passage of an aqueous solution of the complex down a column of Dowex 50W–XS (H⁺ form) resin gave a single product (15) (60%) arising *via* an *endo*-transition state. The stereochemistry of (15) is assigned on the basis of n.O.e. difference spectroscopy. Thus irradiation of the methyl group of (15) causes enhancement of the signals for H_A (11%), H_B (2%), and H_C (7%). Casella *et al.* report a mixture of three diastereoisomeric cycloadducts from this reaction.[9]

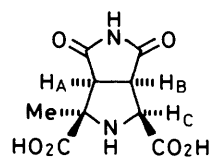The metallo imines (10a–e) and (13) react stereospecifically,

X=Y–ZH $\rightleftharpoons$ X=Y–Z⁻ H⁺

(1)   **(2)**

(3) $\longrightarrow$ **(4)**

(5) $\rightleftharpoons$ **(6)** $\xrightarrow{-H^+}$ $\rightleftharpoons$ **(7)**

X=Y–Z–M^{n+} $\rightleftharpoons$ X=Y–Z⁻ ↓ M$^{(n+1)+}$
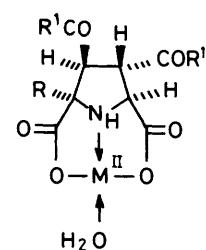
(8)   **(9)**

(10) a ; M = Cu, R = Me
b ; M = Cu, R = Ph
c ; M = Zn, R = Me
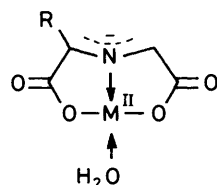d ; M = Zn, R = Ph
e ; M = Cd, R = Me
f ; M = Pb, R = Me

(11)

(12)

(13)

(14)
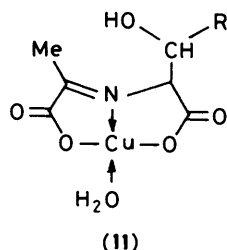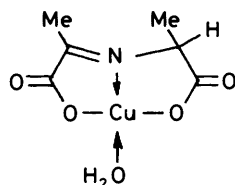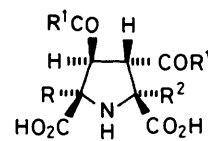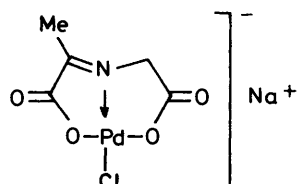
(15)

(16) a; M = Zn
b; M = Cd
c; M = Pb

(17)

Table 1. Cycloadducts derived from metalloimines (10a—f) and (13), and dimethyl fumarate and *trans*-dibenzoylethylene

Adduct	R	R^1	R^2	Yield (%)
(16a)	Me	OMe	—	89
(16a)	Me	Ph	—	80[a]
(16a)	Ph	OMe	—	80
(16b)	Me	OMe	—	90[b]
(17)	Me	OMe	H	63
(17)	Me	Ph	H	60[c]
(17)	Me	OMe	Me	50
(17)	Ph	OMe	H	35

[a] 47:1 Mixture of two isomers. [b] 9:1 Mixture of two isomers. [c] 4.6:1 Mixture of two isomers.

except as noted, with dimethyl fumarate and with *trans*-dibenzoylethylene, to give the cycloadducts (16) (see Table 1). The diamagnetic zinc and cadmium cycloadducts were amenable to direct structural studies by n.m.r. whilst the paramagnetic cycloadduct copper complexes required removal of the metal by passage through a column of Dowex 50W-X8 (H$^+$ form) resin to give (17) (see Table 1). The diamagnetic cycloadduct lead complexes were too insoluble for n.m.r. studies and (14) failed react. In no case could any Michael adduct be detected.

Three of the products in Table 1 are mixtures of two stereoisomers and in two of these cases the dipolarophile involved is *trans*-dibenzoylethylene. Cycloadducts derived from *trans*-dibenzoylethylene contain especially labile protons α to

the ketone groups suggesting that at least in these cases isomerisation of an initial stereospecific cycloadduct might be responsible. Isomerisation could occur in the reaction mixture owing to prolonged reaction times in contact with base and/or Dowex resin. Appropriate experiments demonstrate that both possible causes of isomerisation are operative. Thus, the zinc complex (16a; R = Me, R^1 = OMe) isomerises in pyridine containing 1 mol equivalent of triethylamine at room temperature over 2 days to a 2:1 mixture of (16a; R = Me, R^1 = OMe) and second isomer. Traces of a third isomer are also apparent. Evidence for isomerisation on the Dowex resin is discussed below. The zinc complex (10c) reacts with (18) to give an 18:1 mixture (74%) of (19a) and a minor isomer whilst (10d) and (18) react regio- and stereo-specifically to give a single cycloadduct (19b) (70%). The copper complex (10a) also reacts regiospecifically with (18) to give, after demetallation, the pyrrolidine (20) (50%).

The regiospecificity of the cycloaddition of the metallo-1,3-dipoles (10a, c—e) with the monosubstituted electronegative olefins methyl acrylate, acrylonitrile, and phenyl vinyl sulphone was studied next. The metallo imines (10a) and (10d) react (24 and 6 h respectively) at room temperature with methyl acrylate in pyridine containing 1 mol equivalent of triethylamine to give the appropriate metal complex of a single pyrrolidine (21a; M = Cu^{II}, X=CO$_2$Me, Y=H) and (21b; M=Zn^{II}, X=CO$_2$Me, Y=H) in good yield [70% of the zinc complex and 67% of the demetallated copper complex (23)]. Stereochemical assignments are made on the basis of n.O.e. difference spectroscopy. Thus irradiation ([^{2}H]trifluoroacetic acid) of the methyl group in (23a) caused enhancement of the signals of H$_A$ (14%) and H$_B$ (3%). Similarly (10d) undergoes regio- and stereo-specific cycloaddition (pyridine, 1 mol equivalent of triethylamine, room temperature, 6 h) with acrylonitrile and phenyl vinyl sulphone to give (21b; M=Zn, X=CN, Y=H; 87%) and (21b; M=Zn, X=SO$_2$Ph, Y=H, 80%). In contrast to these regio- and stereo-specific reactions, analogous reactions of (10a, c, and e) with acrylonitrile or phenyl vinyl sulphone give mixtures of epimers of regioisomeric cycloadducts (21) and (22) (Table 2). However, no Michael adducts could be detected.

The regioisomer assignments in Table 2 are made on the basis of the 250 MHz ^{1}H n.m.r. spectra of the reaction mixtures [for Zn^{II} and Cd^{II} complexes] or of the crude demetallated product for Cu^{II} complexes. Thus in the C-3 regioisomers (21) the signal for H$_A$ appears as a triplet whilst in the C-4 regioisomers (22) H$_A$ gives rise to a doublet, e.g. the n.m.r. spectrum (D$_2$O) of the

Table 2. Cycloaddition of metallo-imines and monosubstituted electronegative olefins to give (21) and (22).*

Metalloimine	Olefin	Product ratio[a]		Yield (%)
		C-3 Epimers[d]	C-4 Epimers[d]	
(10a)	Acrylonitrile	13.5:2.5	: 9:1	80[b]
(10a)	Phenyl vinyl sulphone	25.0:0	: 7.5:1	65[b]
(10c)	Acrylonitrile	4.5:1.5	: 6.5:1	80
(10c)	Phenyl vinyl sulphone	4.1:1	: 2.1:0	79
(10e)	Methyl acrylate	2.8:2.1	: 1:0	73
(10e)	Acrylonitrile	12.4:1	: 8.8:4.8	73
(10e)	Phenyl vinyl sulphone	1.25:1	: 1.6:—[c]	75[b]

* Reactions carried out on pyridine containing 1 mol equivalent of triethylamine for 1—2 days at room temperature.
[a] Isomer ratios estimated from 250 MHz n.m.r. spectra. [b] Yield and ratio of demetallated products. [c] A small amount of a fourth isomer appears to be present but is largely obscured by overlapping signals. [d] Major epimers in each case are believed to be those arising from endo-transition states i.e. (21; Y=H) and (22; Y=H)

(18)

(19) a ; R = Me
b ; R = Ph

(20)

(21) a ; R = Me
b ; R = Ph

(22)

(23) a ; R = Me
b ; R = Ph
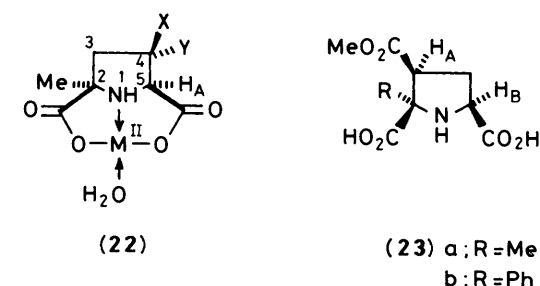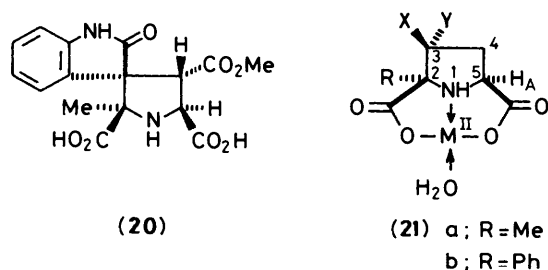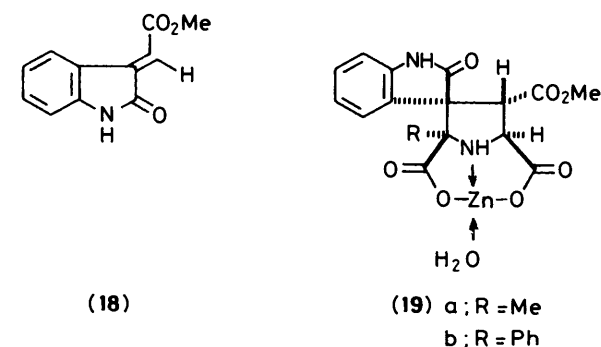
epimeric mixture of (21a; M=Zn[II]) and (22; M=Zn[II]) arising from (10c) and acrylonitrile contains four signals for H_A at δ 3.78(t), 3.90(t), 4.04(d), and 4.00(d) in the ratio 4.5:1.5:6.5:1. Similar n.m.r. patterns are exhibited by the demetallated product mixtures arising from the cycloadduct copper complexes. Casella et al.,[17] studied the reaction of (10a) with methyl acrylate and reported the formation of two isomeric pyrrolidines in the ratio 4:1 after 44 h whilst we only obtained one isomer with a shorter reaction time (24 h). We also observed formation of small amounts of a second isomer in this case when

larger amounts of Dowex resin, or recycled resin was used for the demetallation step. Casella also reports the formation of a 1:1:0.5:0.5 mixture of four isomeric pyrrolidines from the reaction of (10a) and acrylonitrile. However, this latter mixture was erroneously considered to comprise four diastereoisomeric racemates of (24) and the possibility of regioisomers was not considered.

The regio- and stereo-specificity of the cycloadditions of (10d) with methyl acrylate, acrylonitrile, and phenyl vinyl sulphone contrasts with the regio- and stereo-isomeric mixtures produced by (10a), (10c), and (10e) and the same electronegative olefins. However, these results can all be accommodated by a concerted $4\pi + 2\pi$ cycloaddition of the metallo dipole (12) to the monosubstituted electronegative olefins followed by a slower epimerisation of the initial cycloadduct(s). In general, the addition of the metallo dipoles to the monosubstituted electronegative olefins is substantially slower than additions to the 1,2-disubstituted electronegative olefins. The regiochemistry of the cycloaddition of (12) to electronegative olefins will be controlled by the dominant dipole HOMO-dipolarophile LUMO interaction. For the mono-substituted electronegative olefins the largest LUMO coefficient is located on the β-carbon atom (25) whilst for the dipole (12; R = Me) the coefficients at C-1 and C-3 in the HOMO will be essentially equivalent. A concerted $4\pi + 2\pi$ cycloaddition of (12; R = Me) and (25; $X=CO_2Me$, CN or SO_2Ph) is therefore expected to show little regiochemical preference except that imposed by the steric effect

(24)

(25)

(26) a ; M = Zn, R = Ph, X = CO_2Me
b ; M = Zn, R = Me, X = CO_2Me

(27)
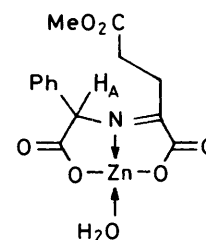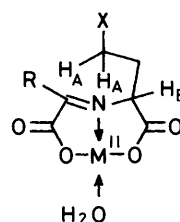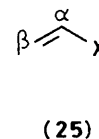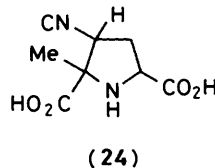
of the methyl substituent at C-1 in (12; R = Me). The regioselectivity with respect to the dipolarophile for the C-3 regioisomer is in the order methyl acrylate ≫ phenyl vinyl sulphone > acrylonitrile with acrylonitrile showing essentially no regioselectivity. However, if the steric effect of the dipolarophile substituent was dominant the expected order would be phenyl vinyl sulphone > methyl acrylate > acrylonitrile. Thus other factors must also be involved. With the dipole (10d) however, the steric blockade of the 1-phenyl substituent is dominant resulting in regiospecific formation of the C-3 isomer (21b). N.m.r. monitoring (by aliquots) of the reaction of (10c) with acrylonitrile shows clear evidence of product isomerisation as the reaction proceeds. This observation and our failure to detect any Michael adducts (26), argue in favour of a concerted $4\pi + 2\pi$ cycloaddition for the reaction of (10) with monosubstituted electronegative olefins. However, Casella has argued in favour of a two-step Michael addition sequence although he was unable to detect any Michael adduct (26). Considering the postulated Michael adduct (26) it is clear that removal of an H_A proton (pK_a ca. 24) from (26) by a weak base such as triethylamine (pK_a ca. 12) would not be expected to occur. Moreover, H_B is the most acidic proton in such complexes. We therefore prepared (26a) and (26b) from glutamic acid half ester and phenylglyoxylic acid or pyruvic acid respectively. When (26a) was kept in dry pyridine containing 1 mol equivalent of triethylamine at room temperature for 8 h it underwent quantitative isomerisation to (27). The isomerisation was readily followed in the n.m.r. spectrum by the disappearance of the signal for H_B (dd) at δ 4.61 due to (26a) and its replacement by a singlet at δ 5.93 due to H_A in (27). No pyrrolidine could be detected. A similar study with (26b) could not be carried out owing to its lack of solubility.

Our conclusions are that the M^{II} complexes of imines derived from α-oxo acids and alanine or glycine undergo concerted stereo-specific cycloadditions. The regiospecificity of these cycloadditions is subject to steric effects and initial cycloadducts can undergo stereoisomerisation if the reaction time is prolonged or if the work-up, via an ion-exchange resin, is not carried out quickly. Short reaction times and use of minimum amounts of fresh ion-exchange resin retard stereoisomerisation.

Experimental

N.m.r. spectra were recorded on Bruker WH90 or Bruker WP250 instruments using tetramethylsilane as internal standard.

I.r. spectra were measured for potassium bromide discs on Perkin-Elmer 157G or 598 instruments. Mass spectra were determined at 70 eV on an MS902 instrument. M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer PE240 automatic analyser. N-(1-Carboxyethylidene)glycinatocopper(II) and N-(α-carboxybenzylidene)glycinatocopper(II) were prepared by a literature method.[18]

Metal Complexes of Imines of α-Amino Acids and α-Oxo Acids: General Procedure.—A suspension of the α-amino acid (0.1 mmol) in 2:1 (v/v) aqueous ethanol (20 ml), was added to pyruvic acid or phenylglyoxylic acid (0.1 mmol). The resultant mixture was stirred at 25 °C for 30 min. by which time it was homogeneous. The appropriate metal acetate (0.1 mmol) in 2:1 (v/v) aqueous ethanol (20 ml) was then added and the mixture stirred at room temperature for 2—4 h during which time the metal complexes were precipitated. The resultant precipitate was collected by suction filtration and dried in vacuo over P_2O_5.

N-(1-*Carboxyethylidene*)glycinatozinc(II) (10c). This was obtained (83.3%) as colourless prisms from water–ethanol, m.p. > 270 °C (Found: N, 5.6. $C_5H_7NO_5Zn$ requires N, 6.15%);

δ (D_2O) 3.93 (s, 2 H, CH_2) and 2.09 (s, 3 H, Me); $v_{max.}$ 3 400br, 1 665, 1 600br, 1 300, and 1 220 cm^{-1}.

N-(α-*Carboxybenzylidene*)glycinatozinc(II) (10d). This was obtained (50%) as colourless plates from water–ethanol, m.p. > 260 °C (Found: C, 41.85; H, 2.9; N, 4.65. $C_{10}H_9NO_5Zn$ requires C, 41.60; H, 3.10; N, 4.80%); δ ([$^2H_5$]pyridine) 6.21 (m, 5 H, ArH) and 3.39 (s, 2 H, CH_2); $v_{max.}$ 3 500br, 1 680, 1 600, 1 440, 1 390, and 1 290 cm^{-1}.

N-(1-*Carboxyethylidene*)glycinatocadmium(II) (10e). This was obtained (60%) as pale yellow prisms from water, m.p. > 250 °C. At 230 °C the colour changed to a deeper yellow (Found: C, 22.0; H, 2.5; N, 5.0. $C_5H_7CdNO_5$ requires C, 21.95; H, 2.55; N, 5.10%); $v_{max.}$ 3 100br, 1 680, 1 630, 1 580br, 1 300, and 1 200 cm^{-1}.

N-(1-*Carboxyethylidene*)glycinatolead(II) (10f). This was obtained (70%) as colourless prisms from water, m.p. > 250 °C (Found: C, 16.55; H, 2.05; N, 3.3. $C_5H_7NO_5Pb$ requires C, 16.30; H, 1.90; N, 3.80%); δ (D_2O), 3.5 (s, 2 H, CH_2), and 1.97 (s, 3 H, Me); $v_{max.}$ 3 400br, 1 660—1 550br, 1 400, and 1 200 cm^{-1}.

Cycloadditions of Metalloimines with 1,2-Disubstituted Electronegative Olefins.—General procedure. The metal complex (10a—f) (10 mmol) as dissolved in dry degassed pyridine (50 ml). Triethylamine (10 mmol) and the dipolarophile (10 mmol) were then added with stirring. The resulting mixture was kept for 4.5—12 h at room temperature during which time the cycloadducts were precipitated. The resultant precipitate was gathered by suction filtration and the filtrate evaporated to dryness under reduced pressure to give a second crop of cycloadduct. The cycloadducts (16; M=Cu^{II}) were dissolved in water (200 ml) and passed through a short column (2 cm diam.) of fresh Dowex 50W-X8 (H$^+$ form) resin (30 g) as quickly as possible. The column was eluted with water (3 l) and the eluant evaporated to dryness under reduced pressure to give (17). The other cycloadducts were crystallized from an appropriate solvent.

3,4-*Bis*(methoxycarbonyl)-2-methylpyrrolidine-2,5-dicarboxylatozinc(II) (16a; R = Me, R^1 = OMe). This was obtained (89%) as colourless needles from water–ethanol, m.p. > 260 °C (Found: C, 34.15; H, 3.7; N, 3.55. $C_{11}H_{15}NO_9Zn\cdot H_2O$ requires C, 34.15; H, 3.80; N, 3.60%); δ(D_2O) 3.95 (d, 1 H, 5-H, J 7.86 Hz), 3.62 (s, 3 H, OMe), 3.56 (s, 3 H, OMe), 3.14 (m, 2 H, 4-H and 3-H), and 1.54 (s, 3 H, 2-Me); $v_{max.}$ 3 400br, 1 730, 1 600br, 1 430, and 1 260 cm^{-1}.

3,4-*Dibenzoyl-2-methylpyrrolidine-2,5-dicarboxylatozinc(II)* (16a; R = Me, R^1 = Ph). This was obtained (75%) as colourless prisms from acetonitrile, m.p. > 250 °C (Found: C, 54.4; H, 4.1; N, 2.8. $C_{21}H_{19}NO_7Zn$ requires C, 54.50; H, 4.10; N, 3.00%); δ[$(CD_3)_2SO$] 7.61 (m, 10 H, ArH), 5.00 (d, 1 H, NH, J 9.23 Hz, exchangeable with D_2O), 4.30 (m, 2 H, 3-H and 4-H), and 3.85 (t, 1 H, 5-H, J 9.13 Hz); $v_{max.}$ 3 400br, 3 300, 1 665, 1 590, and 1 450 cm^{-1}.

Cycloadduct (19a) *obtained from* N-(1-*carboxyethylidene*)glycinatozinc(II) *and the oxindole* (18). The cycloadduct was obtained (74%) as colourless needles from acetonitrile–water, m.p. > 260 °C (Found: C, 43.8; H, 3.8; N, 6.25. $C_{16}H_{16}N_2O_8\cdot 0.5H_2O$ requires C, 43.8; H, 3.65; N, 6.3%); δ[$(CD_3)_2SO$] 10.56 (s, 1 H, NH), 7.03 (m, 4 H, ArH), 4.90 (d, 1 H, NH), 4.11 (dd, 1 H, 5-H), 3.37 (s, 3 H, OMe), 3.22 (d, 1 H, 4-H), and 1.43 (s, 3 H, 2-Me); $v_{max.}$ 3 500—3 300br, 1 730, 1 710, 1 655, 1 620, 1 470, 1 250, and 1 200 cm^{-1}.

Cycloadduct (19b) *obtained from* N-(α-*carboxybenzylidene*)glycinatozinc(II) *and the oxindole* (18). This was obtained (70%) as colourless prisms from acetonitrile, m.p. > 250 °C (material darkened at 210 °C) (Found: C, 51.1; H, 3.65; N, 5.7. $C_{21}H_{18}N_2O_8Zn$ requires C, 51.30; H, 3.65; N, 5.70%); δ[$(CD_3)_2SO$] 10.31 (s, 1 H, NH), 7.23—6.19 (m, 9 H, ArH), 5.32 (d, 1 H, NH), 4.31 (dd, 1 H, 5-H), 3.06 (d, 1 H, 4-H), and 2.82

(s, 3 H, OMe); $\nu_{max.}$ 3 400br, 1 730, 1 700, 1 650, 1 610, 1 470, and 1 230 cm^{-1}.

3,4-Bis(methoxycarbonyl)-2-phenylpyrrolidine-2,5-di-carboxylatozinc(II) (**16a**; R = Ph, R^1 = OMe). This was obtained (80%) as colourless plates from water–ethanol, m.p. >250 °C (decomp.) (Found: C, 49.0; H, 4.3; N, 5.25. C$_{16}$H$_{17}$NO$_9$Zn·H$_2$O·C$_5$H$_5$N requires C, 49.45; H, 4.30; N, 5.50%); δ[(CD$_3$)$_2$SO] 6.42 (m, 5 H, ArH), 3.89 (d, 1 H, NH, exchangeable with D$_2$O), 2.72 (t, 1 H, 5-H), 2.47 (s, 3 H, OMe), 2.46 (d, 1 H, 3-H), 2.25 (s, 3 H, OMe), and 1.89 (t, 1 H, 4-H); $\nu_{max.}$ 3 400br, 1 740, 1 630br, 1 440, and 1 240 cm^{-1}.

3,4-Bis(methoxycarbonyl)-2-methylpyrrolidine-2,5-di-carboxylatocadmium(II) (**16b**; R = Me, R^1 = OMe). This was obtained (90%) as colourless prisms from water–ethanol, m.p. >250 °C. (Found: C, 32.25; H, 3.5; N, 3.3. C$_{11}$H$_{15}$CdNO$_9$ requires C, 32.60; H, 3.60; N, 3.35%); δ(D$_2$O) 4.05 (d, 1 H, 5-H), 3.75 (s, 3 H, OMe), 3.70 (s, 3 H, OMe), and 3.30 (m, 2 H, 3-H and 4-H); $\nu_{max.}$ 3 400br, 1 730, 1 650—1 580br, 1 440, and 1 230 cm^{-1}.

3,4-Bis(methoxycarbonyl)-2-methylpyrrolidine-2,5-di-carboxylic acid (**17**; R = Me, R^1 = OMe, R^2 = H). This was obtained (63%) as colourless needles from water–acetone, m.p. 215—216 °C (Found: C, 45.7; H, 5.2; N, 4.8. C$_{11}$H$_{15}$NO$_8$ requires C, 45.65; H, 5.25; N, 4.85%); δ(CF$_3$CO$_2$D–D$_2$O) 5.44 (d, 1 H, 5-H, J 8.5 Hz), 4.30 (t, 1 H, 4-H), 4.1 (d, 1 H, 3-H, J 10.36 Hz), 4.00 (s, 6 H, 2 × OMe), and 2.15 (s, 3 H, 2-Me); m/z (%) 289 (M^+, 1.5), 272 (0.5), 244 (20), 212 (100), 184 (20), 140 (47), 126 (31), and 108 (27); $\nu_{max.}$ 3 400, 3 110, 1 730, 1 620br, 1 430, and 1 220 cm^{-1}.

3,4-Dibenzoyl-2-methylpyrrolidine-2,5-dicarboxylic acid (**17**; R = Me, R^1 = Ph, R^2 = H). This was obtained (60%) as a 4.7 : 1 mixture of stereoisomers which was not separated (Found: C, 65.95; H, 5.05; N, 3.55. C$_{21}$H$_{19}$NO$_6$ requires C, 66.15; H, 5.00; N, 3.65%). The major isomer is assigned the stereochemistry shown in (**17**; R = Me, R^1 = Ph, R^2 = H); δ[(CD$_3$)$_2$SO–one drop D$_2$O] 7.9—7.38 (m, 10 H, ArH), 4.50 (t, 1 H, 4-H), 4.35 (d, 1 H, 3-H, J 8.50 Hz), and 4.09 (d, 1 H, 5-H, J 8.75 Hz). Minor isomer δ 7.9—7.38 (m, 10 H, ArH), 4.85 (t, 1 H, 4-H), 4.70 (d, 1 H, 5-H, J 9.97 Hz), and 4.44 (d, 1 H, 3-H, J 4.44 Hz); m/z(%) 381 (M^+, 0), 319 (11), 186 (15), 105 (100), 77 (68), 51 (17), and 44 (9); $\nu_{max.}$ 3 450, 3 050, 1 725, 1 710, 1620, 1 480, 1 440, and 1 270 cm^{-1}.

3,4-Bis(methoxycarbonyl)-2,5-dimethylpyrrolidine-2,5-dicarboxylic acid (**17**; R = R^2 = Me, R^1 = OMe). This was obtained (45%) as colourless needles from water, m.p. 210—212 °C (Found: C, 47.5; H, 5.65; N, 4.6. C$_{12}$H$_{17}$NO$_8$ requires C, 47.50; H, 5.65; N, 4.60%); δ(CF$_3$CO$_2$D–one drop D$_2$O) 4.09 (d, 1 H, J 12.03 Hz), 4.01 (d, 1 H, J 12.03 Hz), 3.91 (s, 3 H, OMe), 3.89 (s, 3 H, OMe), 2.12 (s, 3 H, Me), and 1.85 (s, 3 H, Me); m/z (%) 304 (M + 1, 1.5), 258 (41), 226 (100), 154 (81), 122 (40), 115 (32), and 42 (20); $\nu_{max.}$ 3 400br, 3 050, 1 750, 1 730, 1 600br, and 1 250 cm^{-1}.

3,4-Bis(methoxycarbonyl)-2-phenylpyrrolidine-2,5-di-carboxylic acid (**17**; R = Ph, R^1 = OMe, R^2 = H). This was obtained (33%) as colourless prisms from water, m.p. 190 °C (Found: C, 52.55; H, 5.25; N, 4.0. C$_{16}$H$_{17}$NO$_8$·H$_2$O requires C, 52.05; H, 5.15; N, 3.80%); δ(CF$_3$CO$_2$D–one drop D$_2$O 7.65 (br, 5 H, ArH), 5.52 (d, 1 H, 5-H, J 7.16 Hz), 4.85 (d, 3-H, J 6.15 Hz), 4.81 (t, 4-H), 3.96 (s, 3 H, OMe), and 3.83 (s, 3 H, OMe); m/z (%) 351 (M^+, 1.5), 188 (100), 141 (81), 44 (89), 32 (44), 31 (59), and 28 (62); $\nu_{max.}$ 3 450, 1 750, 1 740, and 1 630 cm^{-1}.

Cycloadduct (**20**) *obtained from* N-(1-*carboxyethylidene*)gly-*cinatocopper*(II) *and the oxindole* (**18**). The cycloadduct was obtained (50%) by demetallation of the corresponding Cu^{II} complex. It formed colourless needles from acetonitrile–water, m.p. 187—190 °C (Found: C, 49.95; H, 5.35; N, 6.85. C$_{16}$H$_{16}$N$_2$O$_7$·2H$_2$O requires C, 50.00; H, 5.20; N, 7.10%); δ(CF$_3$CO$_2$D–one drop D$_2$O) 7.59—7.31 (m, 5 H, Ar H), 5.90 (d, 1 H, 5-H, J 7.53 Hz), 4.43 (d, 1 H, 4-H), 3.60 (s, 3 H, OMe), and

1.94 (s, 3 H, 2-Me); $\nu_{max.}$ 3 500—3 300br, 1 730br, 1 610, and 1 470 cm^{-1}.

Cycloadduct (**15**) *obtained from* N-(1-*carboxyethylidene*)gly-*cinatocopper*(II) *and maleimide*. The cycloadduct (60%) was obtained by demetallation of the corresponding Cu^{II} complex. It formed colourless prisms from water–acetone, m.p. 265–266 °C (Found: C, 43.1; H, 4.2; N, 11.2. C$_9$H$_{10}$N$_2$O$_6$·0.5H$_2$O requires C, 43.00; H, 4.00; N, 11.40%); δ(CF$_3$CO$_2$D–one drop D$_2$O) 5.38 (d, 1 H, 5-H, J 9.61 Hz), 4.64 (t, 1 H, 4-H), 4.15 (d, 1 H, 3-H, J 8.62 Hz), and 2.13 (s, 3 H, 2-Me); m/z(%) 242 (M^+, 1), 197 (100), 179 (10), 153 (40), and 126 (21); $\nu_{max.}$ 3 450, 3 220, 1 720, 1 630, 1320, and 1 260 cm^{-1}.

Cycloaddition Reactions of Metalloimines with Monosub-stituted Electronegative Olefins.—General procedure. The metalloimine (**10**) (10 mmol) was dissolved in degassed pyridine to which triethylamine (10 mmol) and the dipolarophile (10 mmol) were added with stirring, and stirring continued for the appropriate time (below).. Cycloadducts (**21b**; M=Zn, X=CO$_2$Me,CN, SO$_2$Ph; Y=H) precipitated from the reaction mixture whilst the other cycloadducts were obtained on removal of the solvent. Copper complexes were demetallated by passage through a short column (2 cm diam.) of fresh Dowex 50W-X8 (H$^+$ form) resin (30g).

Metal Complex	Dipolarophile	Reaction time (h)
(**10d**)	Methyl acrylate	8
(**10d**)	Acrylonitrile	7
(**10d**)	Phenyl vinyl sulphone	8
(**10a**)	Acrylonitrile	24
(**10a**)	Phenyl vinyl sulphone	48
(**10c**)	Acrylonitrile	24
(**10c**	Phenyl vinyl sulphone	48
(**10e**)	Methyl acrylate	24
(**10e**)	Acrylonitrile	48
(**10e**)	Phenyl vinyl sulphone	48
(**10a**)	Methyl acrylate	24

3-Methoxycarbonyl-2-phenylpyrrolidine-2,5-dicarboxylato-zinc(II) (**21b**; M=Zn, X=CO$_2$Me, Y=H). This was obtained (70%) as colourless prisms, from water–ethanol, m.p. >250 °C (Found: C, 44.5; H, 4.05; N, 3.9. C$_{14}$H$_{15}$NO$_7$Zn requires C, 44.90; H, 4.00; N, 3.75%); δ[(CD$_3$)$_2$SO] 7.46—7.09 (m, 5 H, ArH), 4.23 (d, 1 H, NH), 3.63 (m, 1 H, 5-H), 3.30 (s, 3 H, OMe), 3.26 (q, 1 H, 3-H), 2.26 (m, 1 H, 4-H), and 1.80 (m, 1 H, 4-H); $\nu_{max.}$ 3 400br, 1 730, 1 630—1 580br, 1 310, and 1 200 cm^{-1}.

3-Cyano-2-phenylpyrrolidine-2,5-dicarboxylatozinc(II) (**21b**; M=Zn, X=CN, Y=H). This was obtained (87.5%) as colourless prisms, from water–ethanol, m.p. >250 °C (Found: C, 44.05; H, 3.9; N, 8.0. C$_{13}$H$_{12}$N$_2$O$_5$·0.5H$_2$O requires C, 44.50; H, 3.70; N, 8.00%); δ[(CD$_3$)$_2$SO] 7.55—7.3 (m, 5 H, ArH), 5.02 (d, 1 H, NH), 3.89 (m, 1 H, 5-H), 3.52 (dd, 1 H, 3-H), 2.63 (m, 1 H, 4-H), and 1.80 (m, 1 H, 4-H); $\nu_{max.}$ 3 400br, 2 240, 1 660—1 580, 1 400, and 1 220 cm^{-1}.

2-Phenyl-3-phenylsulphonylpyrrolidine-2,5-dicarboxylato-zinc(II) (**21b**; M=Zn, X=SO$_2$Ph, Y=H). This was obtained (80%) as colourless prisms from water–ethanol, m.p. >250 °C (Found: C, 47.05; H, 3.9; N, 3.05. C$_{18}$H$_{18}$NO$_5$Zn requires C, 47.35; H, 3.70; N, 3.05%); δ[(CD$_3$)$_2$SO] 7.5 (m, 10 H, ArH), 4.90 (d, 1 H, NH), 4.40 (m, 1 H, 5-H), 3.76 (dd, 1 H, 3-H), and 2.22 (m, 2 H, 4-H).

3-Methoxycarbonyl-2-methylpyrrolidine-2,5-dicarboxylic acid (**23a**). This was obtained as colourless needles (67%) from water–acetone, m.p. 252 °C (decomp.) (Found: C, 46.4; H, 5.7; N, 6.0. C$_9$H$_{13}$NO$_6$ requires C, 46.75; H, 5.65; N, 6.05%); δ(CF$_3$CO$_2$D) 5.14 (t, 1 H, 5-H), 3.95 (s, 3 H, OMe), 3.75 (t, 1 H, 3-H), 3.39 (m, 1 H, 4-H), and 2.87 (m, 1 H, 4-H); $\nu_{max.}$ 3 420, 1 720, 1 745, and 1 610 cm^{-1}; m/z(%) 232 (M + 1, 0.5), 186 (47), 82 (100), and 44 (44).

3-(4)-Cyano-2-methylpyrrolidine-2,5-dicarboxylic acid. This

was obtained (80%) as a mixture of epimers of regioisomeric cycloadducts (colourless solid) in the ratio 13.5(A):2.5(B):9(C):1(D), by demetallation of the corresponding mixture of copper(II) complexes (Found: C, 47.75; H, 5.2; N, 13.95. $C_8H_{10}N_2O_4 \cdot 0.25 H_2O$ requires C, 47.75; H, 5.20; N, 13.90%); $m/z(\%)$ 154 (15), 153 ($M-CO_2H$, 64), 136 (36), 107 (100), and 44 (79); $\nu_{max.}$ 3 400br, 2 240, 1 720, and 1 600br cm^{-1}; (A) major C-3 epimer $\delta(CF_3CO_2D$–one drop D_2O) 5.20 (t, 1 H, 5-H), 4.2 (t, 1 H, 3-H), 3.14 (m, 2 H, 4-CH$_2$), and 2.22 (s, 3 H, 2-Me); (B) minor C-3 epimer $\delta(CF_3CO_2D$–one drop D_2O) 5.16 (t, 1 H, 5-H), 4.30 (t, 1 H, 3-H), 3.14 (m, 2 H, 4-CH$_2$), and 2.15 (s, 3 H, 2-Me); (C) major C-4 epimer $\delta(CF_3CO_2D$–one drop D_2O) 5.35 (d, 1 H, 5-H), 4.0 (m, 1 H, 4-H), 3.14 (m, 2 H, 3-CH$_2$), and 2.06 (s, 3 H, 2-Me); (D) minor C-4 epimer (CF_3CO_2D–one drop D_2O) 5.45 (d, 1 H, 5-H), 3.9 (m, 1 H, 4-H), 3.14 (m, 2 H, 3-CH$_2$), and 2.05 (s, 3 H, 2-Me).

2-Methyl-3(4)-phenylsulphonylpyrrolidine-2,5-dicarboxylic acid. This was obtained (65%) from the demetallation of the corresponding mixture of Cu complexes as a mixture of epimers of regioisomeric cycloadducts (colourless solid) in the ratio 22.5(A):7.5(B):1(C) (Found: C, 48.55; H, 5.0; N, 4.1. $C_{13}H_{15}NO_6S \cdot 0.5H_2O$ requires C, 44.45; H, 5.00; N, 4.40%); $\nu_{max.}$ 3 450br, 1 725, 1 600br, 1 440, 1 300, 1 150, and 1 080 cm^{-1}. (A) C-3 epimer $\delta(CF_3CO_2D$–one drop D_2O) 7.90 (m, 5 H, ArH), 4.50 (t, 1 H, 5-H), 4.09 (t, 1 H, 3-H), 3.08 (m, 2 H, 4-CH$_2$), and 2.13 (s, 3 H, 2-Me); (B) major C-4 epimer $\delta(CF_3CO_2D$–one drop D_2O) 7.90 (m, 5 H, ArH), 4.76 (d, 1 H, 5-H), 4.35 (m, 1 H, 4-H), 3.08 (m, 2 H, 3-CH$_2$), and 2.11 (s, 3 H, 2-Me); (C) minor C-4 epimer $\delta(CF_3CO_2D$–one drop D_2O) 7.90 (m, 5 H, ArH), 5.0 (d, 1 H, 5-H), 4.3 (m, 1 H, 4-H), 3.08 (m, 2 H, 3-CH$_2$), and 2.06 (s, 3 H, 2-Me).

3(4)-Cyano-2-methylpyrrolidine-2,5-dicarboxylatozinc(II) **(21a)** *and* **(22)** (M=Zn^{II}, X=CN, Y=H and X=H, Y=CN). These were obtained (80%) as a mixture of epimers of regioisomeric cycloadducts (colourless solid) in the ratio 4.5(A):1.5(B):6.5(C):1(D). The n.m.r. spectrum of the isomeric mixture showed separate signals for each isomer as noted below.

(A) major C-3 epimer $\delta(D_2O)$ 3.79 (dd, 1 H, 5-H), 3.00 (t, 1 H, 3-H), 2.26 (m, 2 H, 4-CH$_2$), and 1.26 (s, 3 H, 2-Me); (B) minor C-3 epimer $\delta(D_2O)$ 3.90 (t, 1 H, 5-H), 3.46 (m, 1 H, 3-H), 2.26 (m, 2 H, 4-CH$_2$), and 1.30 (s, 3 H, 2-Me); (C) major C-4 epimer $\delta(D_2O)$ 4.04 (d, 1 H 5-H), 3.52 (m, 1 H, 4-H), 2.26 (m, 2 H, 3-CH$_2$), and 1.18 (s, 3 H, 2-Me); (D) minor C-4 epimer $\delta(D_2O)$ 4.00 (d, 1 H, 5-H), 3.46 (m, 1 H, 4-H), 2.26 (m, 2 H, 3-CH$_2$), and 1.24 (s, 3 H, 2-Me).

The zinc was removed by passage through Dowex 50W-X8 (H$^+$) resin to afford the demetallated material as a colourless solid (Found: C, 46.4; H, 5.2; N, 13.6. $C_8H_{10}N_2O_4 \cdot 0.5H_2O$ requires C, 46.35; H, 5.30; N, 13.50%).

2-Methyl-3(4)-phenylsulphonylpyrrolidine-2,5-dicarboxylato-zinc(II) **(21a)** *and* **(22)** (M=Zn, X=SO$_2$Ph, Y=H and X=H, Y=SO$_2$Ph). This was obtained (79%) as a mixture of epimers of regioisomeric cycloadducts (colourless solid) in the ratio 4.1(A):1(B):2.1(C). Assignments of signals to each isomer were made from the 250 MHz n.m.r. spectrum of the mixture. (A) major C-3 epimer $\delta(D_2O)$ 8.5—7.13 (m, 5 H, ArH), 4.43 (t, 1 H, 5-H), 4.17 (m, 1 H, 3-H), and 3.14—2.34 (m, 2 H, 4-CH$_2$); (B) minor C-3 epimer $\delta(D_2O)$ 8.5—7.13 (m, 5 H, ArH), 5.11 (t, 1 H, 5-H), 4.17 (m, 1 H, 3-H), and 3.14—2.34 (m, 2 H, 4-CH$_2$); (C) C-4 epimer $\delta(D_2O)$ 8.5—7.13 (m, 5 H, ArH), 4.52 (d, 1 H, 5-H), 4.17 (m, 1 H, 4-H), and 3.14—2.34 (m, 2 H, 3-CH$_2$). The mixture of isomers was characterized by removal of zinc by passage through Dowex 50WX8 [H$^+$] resin. The product was a colourless solid (Found: C, 46.7; H, 4.9; N, 3.95. $C_{13}H_{15}NO_6S \cdot H_2O$ requires C, 47.10; H, 5.15; N, 4.20%).

3(4)-Cyano-2-methylpyrrolidine-2,5-dicarboxylato-cadmium(II) **(21a)** *and* **(22)** (M=Cd, X=CN, Y=H and X=H, Y=CN). This was obtained (73%) as a mixture of epimers of

regioisomeric cycloadducts (pale yellow solid) in the ratio 12.4 (A):1(B):8.8(C):4.8(D) (Found: C, 29.0; H, 3.0; N, 8.85. $C_8H_{10}CdN_2O_5$ requires C, 29.40, H, 3.10; N, 8.60%); $\nu_{max.}$ 3 400br, 2 240, and 1 585 cm^{-1}. The n.m.r. spectra of the individual isomers were assigned from the 400-MHz n.m.r. spectrum of the mixture. (A) major C-3 epimer $\delta(D_2O)$ 4.14 (t, 1 H, 5-H), 3.1 (dd, 1 H, 3-H), 2.69 (m, 2 H, 4-CH$_2$), and 1.5 (s, 3 H, 2-Me); (B) minor C-3 epimer $\delta(D_2O)$ 4.0 (t, 1 H, 5-H), 3.16 (dd, 1 H, 3-H), 2.69, (m, 2 H, 4-CH$_2$), and 1.48 (s, 3 H, 2-Me); (C) major C-4 epimer $\delta(D_2O)$ 4.2 (d, 1 H, 5-H), 3.8 (1 H, 4-H), 2.69 (m, 2 H, 3-CH$_2$), and 1.42 (s, 3 H, 2-Me); (D) minor C-4 epimer $\delta(D_2O)$ 4.32 (d, 1 H, 5-H), 3.76 (m, 1 H, 4-H), 2.69 (m, 2 H, 3-CH$_2$), and 1.4 (s, 3 H, 2-Me).

3(4)-Methoxycarbonyl-2-methylpyrrolidine-2,5-dicarboxyl-atocadmium(II) **(21a)** *and* **(22)**, (M=Cd, X=CO$_2$Me, Y=H and X=H, Y=CO$_2$Me). This was obtained (72%) as a mixture of epimers of regioisomeric cycloadducts (colourless solid) in the ratio 2.8(A):2.1(B):1(C) (Found: C, 29.45; H, 3.0; N, 4.2. $C_9H_{13}CdNO_7$ requires C, 29.30; H, 3.85; N, 3.80%); $\nu_{max.}$ 3 400br, 1 725, and 1 580 cm^{-1}. The n.m.r. spectra of the individual isomers were assigned from the 400 MHz n.m.r. spectrum of the mixture. (A) major C-3 epimer $\delta(D_2O)$ 4.26 (t, 1 H, 5-H), 3.98 (t, 1 H, 3-H), 3.7 (s, 3 H, OMe), 2.73 (m, 2 H, 4-CH$_2$), and 1.92 (s, 3 H, 2-Me); (B) minor C-3 epimer $\delta(D_2O)$ 4.2 (t, 1 H, 5-H), 3.92 (t, 1 H, 3-H), 3.6 (s, 3 H, OMe), 2.73 (m, 2 H, 4-CH$_2$), and 1.9 (s, 3 H, 2-Me); (C) C-4 epimer $\delta(D_2O)$ 4.15 (d, 1 H, 5-H), 3.9 (d, 1 H, 4-H), 3.52 (s, 3 H, OMe), 2.73 (m, 2 H, 3-CH$_2$), and 1.94 (s, 3 H, 2-Me).

2-Methyl-3(4)-phenylsulphonylpyrrolidine-2,5-dicarboxylic acid. This was obtained (75%) from the demetallation of corresponding Cd^{II} complexes as a mixture of epimers of regioisomeric cycloadducts (colourless solid) in the ratio 1.25(A):1(B):1.6(C) (Found for the mixture of isomeric cadmium complexes: C, 36.0; H, 3.25; N, 3.15. $C_{13}H_{15}NO_7S \cdot Cd \cdot 0.5H_2O$ requires C, 36.05; H, 3.25; N, 3.25%).

Methyl N-(α-carboxybenzylidene)glutamatozinc(II) **(26a)**. This was prepared by the general procedure above from phenylglyoxylic acid, monomethyl glutamate, and zinc acetate. The product (51%) crystallised from ethanol–water as colourless prisms, m.p. >200 °C (Found: C, 46.0; H, 4.0; N, 3.5. $C_{14}H_{17}NO_7Zn$ requires C, 44.80; H, 4.00; N, 3.75%); $\nu_{max.}$ 3 400br, 1 730, and 1 600br cm^{-1}; $\delta(C_5D_5N)$ 7.35 (m, 5 H, ArH), 4.61 (dd, 1 H, NCH), 2.30 (m, 2 H, CH_2CO$_2$Me), 2.01 (m, 2 H, CH$_2$), and 3.10 (s, 3 H, OMe).

Isomerisation of **(26a)** *to* **(27)**.—A solution of the zinc complex **(26a)** (0.1 mmol) in dry pyridine (50 ml) containing tri-ethylamine (0.1 mmol) was kept at room temperature for 8 h. Removal of the pyridine at room temperature afforded the isomerised product **(27)** as a colourless solid. Crystallization from water afforded colourless prisms, m.p. >200 °C; $\delta([^2H_5]$pyridine) 7.34 (m, 5 H, ArH), 5.92 (s, 1 H, PhCH), 3.41 (s, 3 H, Me), 3.17 (m, 3 H, CH$_2$CH), and 2.54 (m, 1 H, CH); $\nu_{max.}$ 3 400br, 1 735, and 1 600br cm^{-1}.

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