Regioselective Synthesis of 5-Ylidenepyrrol-2(5*H*)-ones by Reaction of Transition Metal-Coordinated Bis(imidoyl) Chlorides with Carbon Nucleophiles

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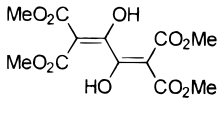
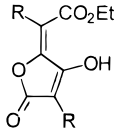
A regioselective transition metal mediated domino reaction of carbon nucleophiles with oxalic acid-bis(imidoyl)chlorides is reported. This reaction provides a convenient access to *E*-configured 5-ylidenepyrrol-2(5*H*)-ones. Without the presence of cobalt(II) or nickel(II) salts, open-chained products were obtained. The regioselective cyclization is controlled by the coordination of the nitrogen atoms of the 1,4-diazadiene system to the transition metal.

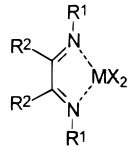
The 1,2-dione unit represents an important structural feature of compounds of pharmaceutical interest[1a] and of materials such as NIR dyes.[1b] 1,2-Diones can be obtained by reaction of oxalyl chloride with carbon nucleophiles. For example, oxalyldimalonic acid derivatives **1a**[2a] and **1b**[2b] have been recently prepared from oxalyl chloride as pharmaceutically relevant analogues of natural pulvinic acid **1c**.[3] Saalfrank and co-workers have reported a self-assembly process of transition and main group metals using deprotonated **1a** as a tetradentate ligand.[2a]



1a



1b (R = CO_2Et)
1c (R = Ph)

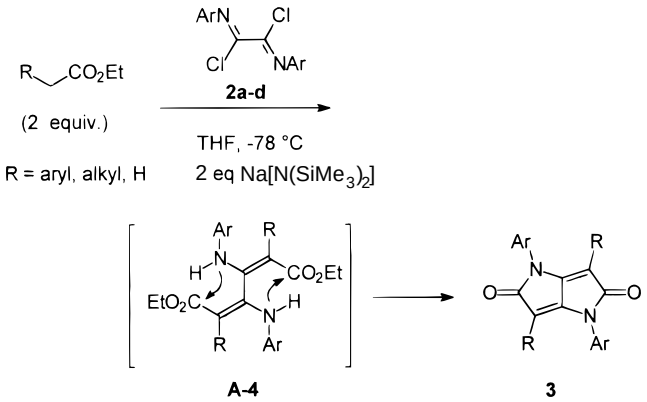


2-MX_2

The development of diimine-ligated transition metal complexes **2-MX_2** as components of efficient catalyst systems for olefin polymerization by Brookhart et al.[4] has given rise to a renewed interest in the chemistry of 1,2-dione-derived 1,4-diazabuta-1,3-dienes. The steric and the electronic properties of these versatile ligands[5] can be fine-tuned by varying the substituents at the nitrogens and at the internal carbon atoms of the diazabutadiene backbone.

En route to the development of new syntheses of functionalized 1,4-diazabutadienes and of azaanalogues of heterocycles **1b,c**, we are interested in the reaction of oxalic acid-bis(imidoyl)chlorides $C_2Cl_2(NAr)_2$ **2** with carbon nucleophiles.[6] Recently, we have reported the formation of pyrrolo[3,2-*b*]pyrrole-2,5-diones **3**, azaanalogous derivatives of pulvinic acid, by reaction of **2** with carbanions of alkyl- and aryl-substituted acetic esters via bisenamine intermediates **A-4** (Scheme 1).[7] These reactions involve attack of the nitrogen atoms on the ester carbonyl groups. Cyclization can, in principle, occur not only by attack of a nitrogen atom but also by attack of a carbon atom on the ester group. Herein, we report full details of a new C-regioselective cobalt(II)-mediated cyclization which provides a convenient access to 5-ylidenepyrrol-2(5*H*)-ones **5**.[8] In addition, experiments related to questions of the mechanism and the preparation of azaanalogues of oxalyldimalonic acid derivatives **1a** are reported.

Scheme 1



Results and Discussion

Reaction of bis(imidoyl)chlorides **2a**−**b**,**d** (1.0 equiv) with sodium diethyl malonate (2.0 equiv) (generated by means of 2.0 equiv of $Na[N(SiMe_3)_2]$) in the presence of

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Table 1

entry	2	5	R	Ar	additive (equiv)[b]	λ_1[c]	λ_2	λ_3	percent[a]
1	**a**	**a**	CO_2Et	Tol	$CoCl_2$ (1)	273 (4.01)	340 (3.94)		54
2	**b**	**b**	CO_2Et	Ph	$CoBr_2$ (1)	270 (3.96)	341 (3.91)		61
3	**d**	**c**	CO_2Et	*p*-$(NO_2)C_6H_4$	$CoBr_2$ (1)	324 (4.26)	368 (4.28)		56
4	**a**	**d**	CN	Tol	$CoBr_2$ (1)	266 (3.82)	365 (4.09)	417 (4.16)	71
5	**a**	**d**	CN	Tol	$CoBr_2$ (2)				68
6	**a**	**d**	CN	Tol	$CoBr_2$ (cat.)				0[d]
7	**a**	**d**	CN	Tol	$NiBr_2$ (1)				73
8	**a**	**d**	CN	Tol	$BF_3{\cdot}OEt_2$ (1)				0
9	**b**	**e**	CN	Ph	$CoBr_2$ (1)	260 (3.82)	362 (4.12)	408 (4.19)	74
10	**c**	**f**	CN	*p*-$(MeO)C_6H_4$	$CoCl_2$ (1)	269 (3.86)	340 (3.99)	413 (4.12)	66
11	**e**	**g**	CN	Tosyl	$CoBr_2$ (1)				0

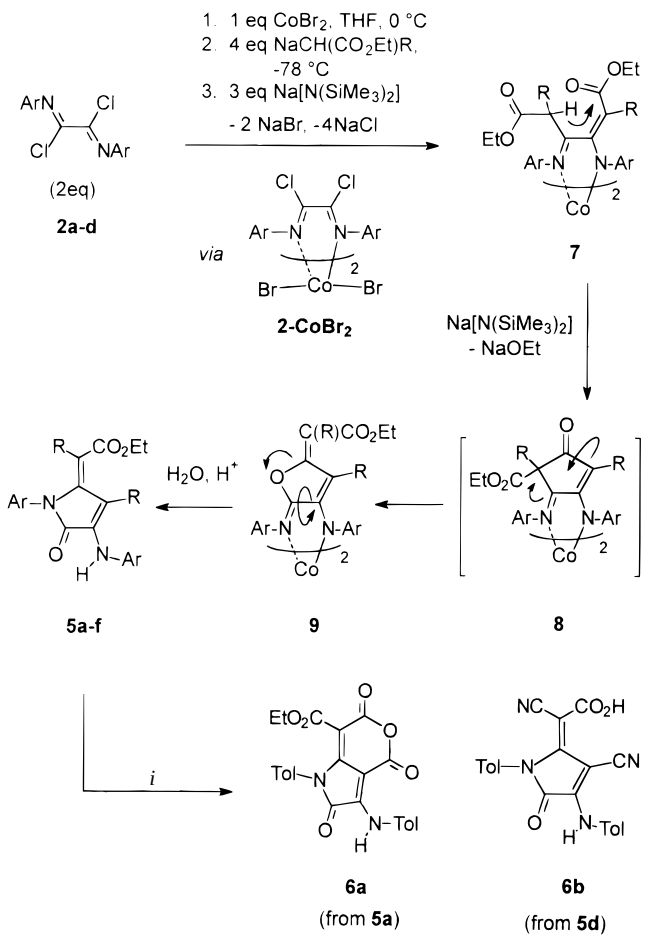
[a] Isolated yield. [b] Equivalents related to 2 equiv of **2**. [c] UV/vis [nm] (acetonitrile). [d] Formation of an open-chained product.

cobalt(II) or nickel(II) salts and an excess of Na[N-$(SiMe_3)_2$] (1.5 equiv) resulted in regioselective C-cyclization to give 5-ylidenepyrrol-2(5*H*)-ones **5a**−**c** in generally good yields (54−61%). Reaction of **2a**−**c** with sodium ethyl cyanoacetate proceeded equally well to give *E*-configured 5-ylidenepyrrol-2(5*H*)-ones **5d**−**f** (66−74%). To prepare the N-deprotected heterocyclic core structure, sodium ethyl cyanoacetate was reacted with tosyl-substituted bis(imidoyl)chloride **2e**. Unfortunately, this reaction resulted in formation of a complex product mixture (Table 1, entry 11). Similarly, the use of benzyl derivatives of **2** was not successful. In case of the yellow colored triesters **5a**−**c** the $\pi \rightarrow \pi^*$ transitions (λ_2) are observed at ca. 340 nm. Auxochromic effects are observed for λ_2 when two of the three ester functions are replaced by cyano groups and additional $\pi \rightarrow \pi^*$ transitions (λ_3) are detected (Table 1).

It is noteworthy, that employment of $BF_3{\cdot}OEt_2$ rather than $CoBr_2$ resulted in decomposition rather than in cyclization (Table 1, entry 8). No cyclization but formation of open-chained products was observed in the reaction of ethyl cyanoacetate with **2a** when only catalytic amounts of cobalt(II) bromide were used (entry 6). In contrast, cyclization was observed when 2 equiv of $CoBr_2$ rather than only 1 was employed (entry 5). The reaction proceeded equally well with $NiBr_2$ instead of $CoBr_2$ (entry 7).

Formation of 5-ylidenepyrrol-2(5*H*)-ones **5** can be rationalized by the following mechanism (Scheme 2): A cobalt(II)−1,4-diazadiene complex (**2-CoBr$_2$**) is initially formed by complexation of $CoBr_2$ with bis(imidoyl) chlorides **2**. Attack of the carbanion on **2-CoBr$_2$** affords the 3-amino-1-azadiene complex **7**[9] which undergoes a ring closure reaction to give intermediate **8** (being an unstable tetracarbonylmethane derivative). Rearrangement of the latter to **9**, subsequent Dimroth rearrangement (before or after decomplexation), and aqueous work up finally afford 5-ylidenepyrrol-2(5*H*)-ones **5a**−**f**. A related compound has been previously prepared in a multistep procedure in low overall yield (ca. 10%).[2b]

Scheme 2[a]



[a] Reagents and conditions: *i* 1. KOH/H_2O (1 mol/L), 30 min, 50 °C; 2. HCl (2 mol/L). Yields: **6a**, 72%; **6b**, 70%.

Experiments to explore the reactivity of heterocycles **5** were first carried out. Treatment of **5a** with potassium hydroxide gave the bicyclic anhydride **6a** (72%) containing a new heterocyclic core structure. It is noteworthy that only two of the three ester groups are selectively hydrolyzed under the reaction conditions employed. Treatment of the monoester **5d** with potassium hydroxide resulted in saponification of the ester group to give the acid **6b** (70%).

The structures of both **5a** and **5d**[8] were independently confirmed by X-ray analyses. The aryl groups of **5a** and **5d** are twisted out of plane. The bond lengths C1−N1, C2−N2, and N1−C4 are decreased relative to C−N single bonds due to the resonance within the amide and the vinylogous amide functions. Bond length alternation is

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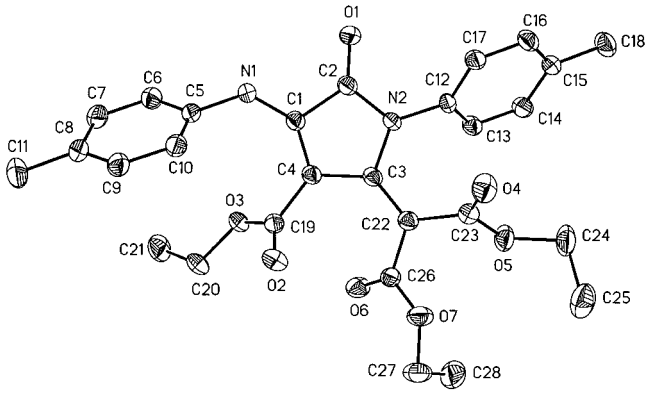

Figure 1. ORTEP plot of **5a** with the atom numbering scheme referred to in the text. The thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms. Selected bond lengths [Å] and angles [deg]: O1−C2 1.209(2), N1−C1 1.339(3), N2−C3 1.417(2), C1−C4 1.369(3), C5−C6 1.381(3), N1−C5 1.425(2), N2−C2 1.374(3), C1−C2 1.498(3), C3−C4 1.461(3); C1−N1−C5 127.6(2), C2−N2−C3 110.4(2), N1−C1−C2 115.6(2), O1−C2−N2 126.9(2), N2−C2−C1 106.4(2), C1−C4−C3 108.4(2), C5−C6−C7 119.4(2), N1−C1−C4 136.4(2), C4−C1−C2 107.9(2), O1−C2−C1 126.7(2), N2−C3−C4 106.8(2), C6−N5−N1 118.9(2)

Scheme 3

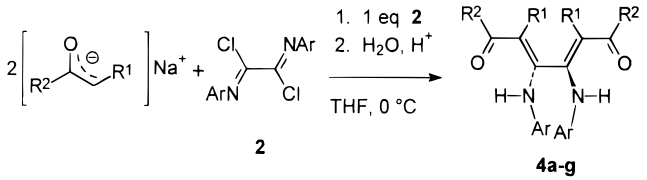

Table 2

2	4	R^1	R^2	Ar[a]	$\delta_{(N-H)}$[b]	percent[c]
f	**a**	CO_2Et	OEt	Ar^1		20
a	**b**	CN	Ph	Tol	13.35	14
a	**c**	CN	OEt	Tol	11.29	72
b	**d**	CN	OEt	Ph	11.38	48
a	**e**	CN	$N(CH_2)_5$	Tol	8.36	56
a	**f**	CN	$N(CH_2)_4O$	Tol	8.73	36
e	**g**	CN	OEt	Tosyl		40

[a] Ar^1 = *m*-ClC_6H_4; Tol = *p*-MeC_6H_4; $N(CH_2)_5$ = piperidinyl; $N(CH_2)_4O$ = morpholinyl. [b] ^1H NMR (200 MHz, CD_2Cl_2). **4f**: DMSO-d_6. [c] Isolated yield.

observed for the heterocyclic five-membered ring. Interestingly, investigation of the crystal lattice showed that for **5a**, which was crystallized from toluene, a dimeric structure was formed. Two hydrogen bonds are located between the atoms N1 and O1 of two molecules of **5a**. A monomeric structure was observed for **5d**. In this case, the hydrogen bond was located between the heterocyclic nitrogen atom and the oxygen atom of the solvent (DMF).

For comparison, reactions of bis(imidoyl) chlorides with carbon nucleophiles without addition of metal salts were carried out (Scheme 3, Table 2). In these reactions open-chained rather than C- or N-cyclization products were obtained. Treatment of sodium diethyl malonate Na[CH-$(CO_2Et)_2$] with bis(*m*-chlorophenylimidoyl)chloride **2f** gave bis-enamine **4a** in low yield.[10] Reaction of bis-(imidoyl)chlorides **2a,b** with sodium benzoyl acetonitrile and sodium ethyl cyanoacetate at 0 °C afforded bis-enamines **4b**−**d** (48−72%). Reaction of *N*-(cyanoacetyl)-

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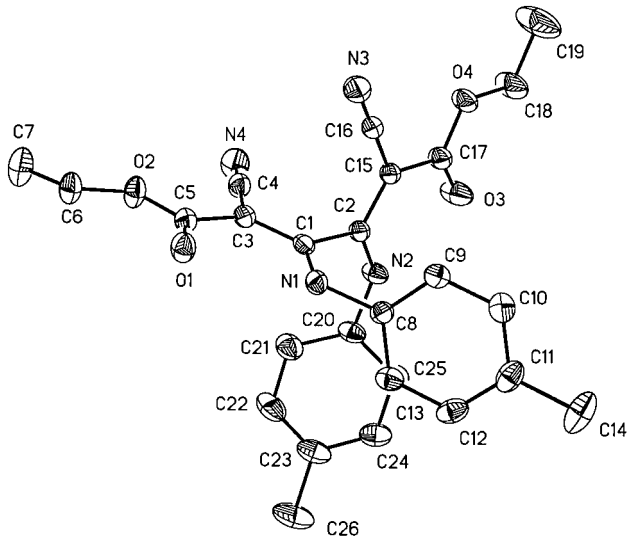


Figure 2. ORTEP plot of **4c** with the atom numbering scheme. The thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms. Selected bond lengths [Å] and angles [deg]: O1−C5 1.216(2), O2−C6 1.457(2), N1−C1 1.329(2), N1−C8 1.437(2), C1−C3 1.383(2), C3−C5 1.461(2), O2−C5 1.333(2), N4−C4 1.147 (2), C1−C2 1.505(2), C3−C4 1.428 (2); C5−O2−C6 116.4(1), C1−N1−C8 123.9(1), N1−C1−C3 125.5(1), C1−C3−C4 119.2(1), O1−C5−O2 124.8(1)

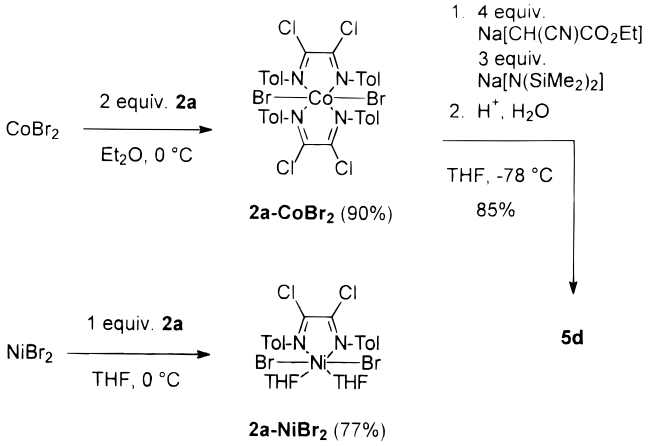
piperidine and -morpholine afforded bis-enamines **4e** and **4f** (56% and 36%, respectively). Tosyl-derivative **4g** was isolated in the reaction of bis(imidoyl)chloride **2e** with ethyl cyanoacetate.

According to the ^1H and ^{13}C NMR spectra of **4**, symmetrical structures are adopted in solution. As indicated by the low-field shifts (^1H NMR) of the respective N−H hydrogens that isomers containing intramolecular hydrogen bonds (N−H···O) are present. It is noteworthy the configuration of these isomers is different from that of intermediates **A-4** (Scheme 1). The resonance of the intramolecular hydrogen bond (N−H···O) of the amide **4e** is shifted upfield relative to the resonances of the esters **4c,d**. The N−H resonances of the esters are shifted upfield relative to the respective resonance of the ketone **4b**.

X-ray diffraction of **4c** exhibits cis geometry of the double bonds in the solid state, and thus two intramolecular hydrogen bonds are observed (H···O distances, 2.085 and 1.895 Å) (Figure 2). The diene system is twisted out of plane (torsion angle N1−C1−C2−N2, 79.8°), and a π-stacking interaction is observed for the aryl groups (distance C20/21/24/25 to C8−13, 3.533 Å). The bond length C1−C3 is increased with respect to olefinic double bonds and C3−C5 is shortened relative to alkyl-substituted C−C single bonds due to the amide resonance within the vinylogous amide function.

It is noteworthy that 2:1 products were also formed when the starting materials were mixed in a 1:1 stoichiometry. On the other hand, reflux of **4c** and **4d** in toluene resulted in formation of complex reaction mixtures from which C-cyclization products **5d** and **5e** were isolated in low yields (26 and 22%, respectively). This cyclization is not possible from the configuration present in educts **4c,d**. Thus, an at least small amount of other isomers appears to be present under the reaction conditions employed. This is supported by AM1 calculations[11] of the energies of possible tautomers of **4c** (Supporting Information). Due to the presence of an ester group in

Scheme 4



trans relationship to the amino group in case of bis-enamine **4a**, condensation via 2-fold attack of the nitrogen atoms on the ester groups took place by boiling of **4a** in diphenyl ether.[10] No cyclization was induced when diketodiene **4c** was treated with $Na[N(SiMe_3)_2]$.

To elucidate the mechanism of the transition metal mediated synthesis of 5-ylidenepyrrol-2(5*H*)-ones **5**, the complexation of transition metals with bis(imidoyl)-dichlorides **2** was studied (Scheme 4). Treatment of an ether solution of $C_2Cl_2(NTol)_2$ (**2a**) with cobalt(II) bromide afforded the novel red cobalt(II) complex **2a-CoBr$_2$** (90%). Likewise, reaction of **2a** with nickel(II) bromide in THF gave the red nickel(II) complex **2a-NiBr$_2$** (77%). Treatment of **2a-CoBr$_2$** (1 equiv) with sodium ethyl cyanoacetate (4 equiv) and $Na[N(SiMe_3)_2]$ (3 equiv) and subsequent aqueous workup afforded 5-ylidenepyrrol-2(5*H*)-one **5d** in high yield (85%).

The cobalt atom of complex **2a-CoBr$_2$** is coordinated by two bis(imidoyl)chloride molecules, whereas the nickel atom of complex **2a-NiBr$_2$** is coordinated by only one bis-(imidoyl)chloride unit and by two THF molecules. As shown by the crystal structure of **2a-NiBr$_2$** (Figure 3), the coordinated dielectrophile exhibits *s-cis* configuration due to chelation of the 1,4-diazadiene system to the metal. In contrast, the free ligand $C_2Cl_2(NAr)_2$ has *s-trans* geometry.[12] The nickel atom exhibits an octahedral coordination sphere. The bromine atoms are located trans to each other, and the THF molecules are located cis to each other. The C1−C2 distance (1.516 Å) and the C−N distance (1.225 Å) of the imino groups in **2a-NiBr$_2$** are similar to those of noncoordinated $C_2Cl_2(NAr)_2$ **2g** (Ar = 2,6-bis-isopropylphenyl) (1.495 and 1.239 Å, respectively). The bond lengths Ni−N of **2a-NiBr$_2$** (2.088, 2.111 Å) are increased with respect to those of the known dimeric complex $[(tDAB)NiBr_2]_2$ (2.039, 2.042 Å) and of the monomeric complex $[(tDAB)NiBr_2]$ (1.996, 2.002 Å) (tDAB = *N*,*N*-di-*tert*-butyldiazabutadiene).[13] This effect can be explained by the decreasing coordination number of nickel(II) in this series (from 6 over 5 to 4). The coordination of $C_2Cl_2(NTol)_2$ to the metal is only weak and the ligand is readily replaced by pyridine or TMEDA in ligand exchange reactions.

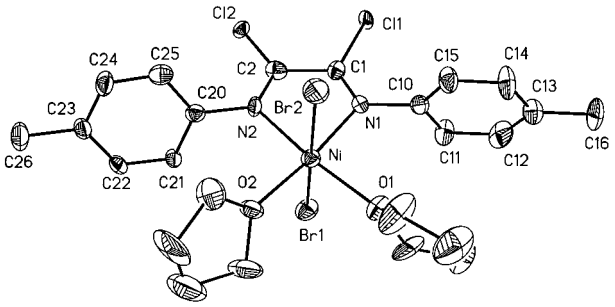
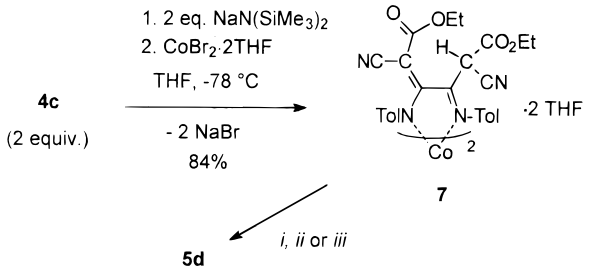


Figure 3. ORTEP plot of **2a-NiBr$_2$** with the atom numbering scheme. The thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms. Selected bond lengths [Å] and angles [deg]: Ni1−Br1 2.535(3), Ni1−Br2 2.517(3), Ni1−O1 2.127(13), Ni1−O2 2.095(12), C1−N1 1.225(22), C2−N2 1.280-(22), Ni1−N1 2.088(14), Ni1−N2 2.111(14), C1−Cl1 1.788(18), C2−Cl2 1.751(19), N1−C10 1.471(22), N2−C20 1.469, C1−C2 1.516(25); Br1−Ni−N1 88.3(4), Br1−Ni−N2 87.0(4), Br1−Ni−O1 92.2(4), Br1−Ni−O2 94.1(3), O2−Ni−N1 174.0(5), O1−Ni−N2 97.7(5), C1−C2−Cl2 121.5(13), C1−N1−C10 120.8(15), Br1−Ni−Br2 173.8(1), O1−Ni−O2 89.2(5), Br2−Ni−N1 86.4-(4), Br2−Ni−O1 91.7(4), N1−C1−Cl1 126.1(14), N1−C1−Cl1 126.1(14), Ni−N(1)−C10 122.8(10)

Scheme 5[a]



[a] Reagents and conditions: (i) H^+, H_2O, 41%. (ii) 1. cat. $Na[N(SiMe_3)_2]$, THF, −78 °C; 2. H^+, H_2O, 89%. (iii) 1. 3 equiv of $Na[N(SiMe_3)_2]$, THF, −78 °C; 2. H^+, H_2O, 87%.

Bis-enamine **4c** was deprotonated using $Na[N(SiMe_3)_2]$ and was reacted with $CoBr_2$·2THF to form cobalt(II) complex **7** in 84% yield (Scheme 5). Two molecules each of **4c** and of THF are coordinated to the metal. Hydrolysis of **7** provided 5-ylidenepyrrol-2(5*H*)-one **5d** in 41% yield. The yield was increased when catalytic or stoichiometric amounts of $Na[N(SiMe_3)_2]$ were added to a THF solution of **7** at −78 °C before hydrolytic workup, and **5d** was isolated in 89 and 87% yield, respectively.

The aqueous workup of the domino reaction was replaced by filtration of the reaction mixture through a layer of Celite (Scheme 6). Crystalization afforded nickel-(II) complexes **9a,b**. The elemental analyses and mass spectra of these compounds suggested that structures I or II are adopted. Deprotonation of **5d** using $Na[N(SiMe_3)_2]$ and subsequent treatment with $CoBr_2$·2THF or $NiBr_2$·DME gave stable metal complexes of type II (Supporting Information). Although the definite structure of **9a,b** could not be unambigiously determined, the isolation of these intermediates showed that an excess of $Na[N(SiMe_3)_2]$ (as present in this experiment) is mandatory for the transformation of **7** into **9** in high

(11) The configurations of the isomers of **4c** were generated and the energies were subsequently minimized using the MM+ force field which is implemented in release 3.0 of HyperChem. MM+ supplements the standard MM2 parameters (Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127). All input geometries were taken from the molecule editor and optimized using the Polak-Ribiere algorithm. The minima obtained from the search were further optimized using the AM1 wave function (Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902) and the RHF approximation.

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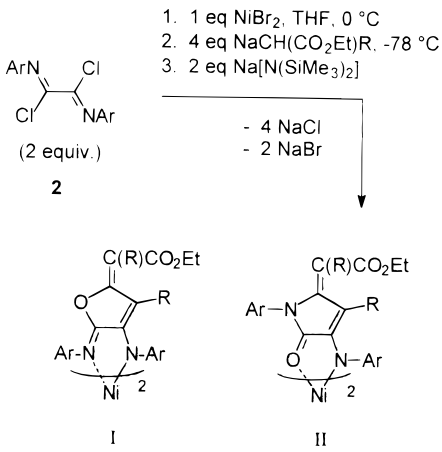
Scheme 6



9a (Ar = Tol, R = CO_2Et)
9b (Ar = *p*-(MeO)C_6H_4, R = CN)

yield. Since no excess of base was present during the reaction of deprotonated **4c** with $CoBr_2$ (Scheme 5) complex **7** could be isolated. Upon treatment with base and subsequent hydrolysis this compound could be converted into 5-ylidenepyrrol-2(5*H*)-one **5d**.

In summary, we have found a transition metal mediated domino reaction which regio- and stereoselectively afforded 5-ylidenepyrrol-2(5*H*)-ones **5**. The variation of the amount and the type of the metal salts, the isolation of intermediates **2-MBr$_2$**, **7**, and **9**, and their conversion into **5d** suggest that six steps (C−C coupling, complexation, Dieckmann condensation, rearrangement, Dimroth rearrangement, decomplexation) are involved in the domino reaction. The regioselectivity is presumably controlled by the conformational lock of the 3-amino-1-azadiene ligand by complexation of the nitrogen atoms which are, thus, not available for intramolecular attack on the ester groups. A base-catalyzed mechanism or the simple action of the transition metal salts as a Lewis acid are less likely. For an effective cyclization, stoichiometric amounts of the metal and, at least, a catalytic excess of base are required.

The 5-ylidenepyrrol-2(5*H*)-one structural unit **5** is found in a range of biologically important natural products including holomycin,[14a] pukeleimide A,[14b] isoampullicin,[14c] and the bile pigment bilirubin.[14d] Although synthetic routes to the corresponding 5-ylidenefuran-2(5*H*)-ones and 4-ylidenetetronic acids are well documented,[15] only few synthetic studies toward 5-ylidenepyrrol-2(5*H*)-ones **5** have been published.[16] The convenient preparation of 2,3-diamino-1,3-butadienes **4** (which represent azaanalogues of oxalyldimalonic acid derivatives **1a)** points the way to a novel entry into bis-heterocyclic structures and β-amino acids. Bis(imidoyl)chlorides **2**, bisenamines **4**, and 5-ylidenepyrrol-2(5*H*)-ones **5** are readily coordinated by transition metals, an interesting feature in view of the development of new ligands for olefin polymerization catalysis.

Experimental Section

General. All solvents were dried by standard methods, and all reactions were carried out under an inert atmosphere. Petroleum ether (bp 40−70 °C) and ether were distilled prior to use. The oxalic acid-bis(imidoyl) dichlorides **2** were prepared by literature procedures.[12] NMR spectra were recorded at 200 and 50 MHz (for ^{1}H and ^{13}C, respectively), if not quoted otherwise. For ^{1}H NMR, $CDCl_3$ and CD_2Cl_2 (TMS as internal standard), DMSO-d_6 (δ = 2.49), THF-d_8 (δ = 1.73, 3.58), DMF-d_7 (δ = 2.90, 8.02), and acetone-d_6 (δ = 2.04) were used as solvents. For ^{13}C NMR, $CDCl_3$ and CD_2Cl_2 (TMS as internal standard), DMSO-d_6 (δ = 39.5), THF-d_8 (δ = 25.5, 67.7), DMF-d_7 (δ = 29.7, 34.8), and acetone-d_6 (δ = 29.8, 206.3) were used as solvents. The multiplicity of the C atoms was determined by the DEPT 135 technique and quoted as CH_3, CH_2, CH, and C for primary, secondary, tertiary, and quaternary carbon atoms, respectively. Mass spectra were recorded using the electron ionization (70 eV) or the chemical ionization method (CI with water). For preparative scale chromatography, silica gel (60−200 mesh) was used. Melting points are uncorrected and elemental analyses were performed at the microanalytical laboratory of the University of Jena.

X-ray Diffraction Data. The intensity data were collected using graphite-monochromated Mo Kα radiation. The crystals were mounted in a cold nitrogen stream at −90 °C. Data were corrected for Lorentz and polarization effects, but not for absorption.[17] The structures were solved by direct methods (SHELXS)[18] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[19] The hydrogen atoms were included at calculated positions with fixed thermal parameters for **2a-NiBr$_2$** while the hydrogen atoms of **4c** and **5a** were located from the difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically. Crystallographic details are listed in Table 3.

General Procedure for the Preparation of Bisenamines (4b−f). To a THF solution (20 mL) of the respective cyanoacetic derivatives or benzoylacetonitrile (10 mmol) was added 10 mL of $NaN(SiMe_3)_2$ (1 M solution in THF) in 25 mL of THF. After 10 min of stirring at 0 °C, the suspension was transferred to a THF solution (25 mL) of the respective oxalic acid-bis(imidoyl) dichloride (**2a**, 1.5 g; **2b**, 1.2 g; 5 mmol) at −20 °C. The cooling bath was removed, and the reaction mixture was stirred at 50 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into an aequous solution of 300 mL of NH_4Cl which was extracted with ether/THF (1:1). The combined organic layers were dried (Na_2SO_4) and filtered and the solvent was removed in vacuo. To the residue was added 2 mL of methanol. The precipitated product was washed twice with methanol and was dried in vacuo.

***(Z,Z)*-1,4-Dicyano-2,3-di(*p*-tolyl)aminobutadiene-1,4-bis(phenyl ketone) (4b).** Starting with benzoyl acetonitrile (0.5 g, 3.4 mmol) and **2a** (0.5 g, 1.7 mmol), 125 mg of **4b** (14%) was isolated as yellow crystals (mp 308−310 °C). IR (Nujol): $\bar{\nu}$ 2199 (s) cm^{-1}, 1612 (s), 1591 (s), 1570 (s), 1514 (s), 1494 (m). ^{1}H NMR (CD_2Cl_2): δ 2.38 (s, 6 H, Tol-CH_3), 6.98 (d, J = 8.4 Hz, 4 H, Ar), 7.20 (d, J = 8.3 Hz, 4 H, Ar), 7.56 (m, 6 H, Ar), 7.85 (d, J = 8.0 Hz, 4 H, Ar), 13.35 (s, 2 H, NH). ^{13}C NMR (CD_2Cl_2): δ_C 21.2 (Tol-CH_3), 85.6 (C, *C*CN), 118.8 (C, CN), 123.5, 128.7, 130.6, 132.8, 133.9, 138.5, 139.1 (CH, C, Ar), 159.4 (C, *C*NHTol), 193.3 (CO). MS (CI, H_2O) *m*/*z* (%): 523 (22) [M^+ + 1], 416 (26), 261 (4) [M^+/2]. Anal. Calcd for $C_{34}H_{26}N_4O_2$ (522.6): C, 78.14; H, 5.01; N, 10.72. Found: C, 77.71; H, 5.03; N, 10.52.

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Table 3

compd	4c	2a-$NiBr_2$	5a
empirical formula	$C_{26}H_{26}N_4O_4$	$C_{24}H_{30}Br_2Cl_2N_2NiO_2$	$C_{28}H_{30}N_2O_7$
fw	458.5	667.9	506.5
cryst size [mm^3]	0.40 × 0.40 × 0.38	0.50 × 0.40 × 0.40	0.40 × 0.38 × 0.20
cryst color and habit	yellow prism	red columns	yellow prism
cryst syst	triclinic	orthorhombic	monoclinic
space group	*P*1	*Pbca*	$P2_1/c$
unit cell dimens [Å, deg]	$a = 10.716(2)$	$a = 10.004(2)$	$a = 8.841(1)$
	$b = 11.423(2)$	$b = 16.443(4)$	$b = 19.805(2)$
	$c = 11.799(2)$	$c = 33.812(11)$	$c = 14.815(2)$
	$\alpha = 89.68(3)$	$\alpha = 90$	$\alpha = 90$
	$\beta = 72.59(3)$	$\beta = 90$	$\beta = 101.89(1)$
	$\gamma = 62.43(3)$	$\gamma = 90$	$\gamma = 90$
vol [$Å^3$]	1206.4(4)	5562(3)	2538.4(5)
Z	2	8	4
density (calcd) [g cm^{-3}]	1.26	1.595	1.32
μ (Mo Kα) [cm^{-1}]	0.87	0.38	0.96
F(000)	484	2688	1072
2Θ range for data collection [deg]	2.28, 29.97	1.5, 27	2.35, 29.84
reflns collect in $\pm h, \pm k, +l$	7101	8401	7637
indep reflns	6800	6108	6898
reflns with $F_o > 4\sigma(F_o)$	4983	1881	4672
final *R* indices	$R = 0.046$	$R = 0.0598$	$R = 0.047$
	$wR^2 = 0.118$	$wR^2 = 0.076$	$wR^2 = 0.106$
GOF	1.13	7.74	1.22
largest diff peak [$eÅ^{-3}$]	0.49	1.16	0.34

(*Z*,*Z*)-1,4-Dicyano-2,3-di(*p*-tolyl)aminobutadiene-1,4-dicarboxylic Acid Diethyl Ester (4c). Starting with ethyl cyanoacetate (1.1 mL, 10 mmol) and **2a** (1.5 g, 5 mmol), 3.3 g of **4c** (72%) was isolated as yellow crystals (mp 196−199 °C). IR (Nujol): $\bar{\nu}$ 3322 (m) cm^{-1}, 2213 (s), 1670 (s), 1595 (s). ^{1}H NMR (CD_2Cl_2): δ 1.35 (t, $J = 7.2$ Hz, 6 H, CH_2CH_3), 2.34 (s, 6 H, Tol-CH_3), 4.27 (m, $J = 7.2$ Hz, 4 H, CH_2CH_3), 6.87, 7.13 (d, $J = 8.5$ Hz, 8 H, Tol), 11.29 (s, 2 H, NH). ^{13}C NMR (CD_2Cl_2): δ_C 14.4 (CH_2CH_3), 21.1 (Tol-CH_3), 62.3 (CH_2CH_3), 77.4 (C, *C*CN), 116.0 (C, CN), 123.2, 130.4 (CH, Tol), 134.0 (C, Tol-C to C), 138.4 (C, Tol-C to N), 157.9 (C, *C*NHTol), 167.2 (CO). MS (EI) *m*/*z* (%): 458 (19) [M^+], 385 (57), 339 (100), 229 [M^+/2]. Anal. Calcd for $C_{26}H_{26}N_4O_4$ (458.5): C, 68.11; H, 5.72; N, 12.22. Found: C, 68.52; H, 5.79; N, 11.97.

(*Z*,*Z*)-1,4-Dicyano-2,3-di(phenyl)aminobutadiene-1,4-dicarboxylic Acid Diethyl Ester (4d). Starting with ethyl cyanoacetate (1.1 mL, 10 mmol) and **2b** (1.35 g, 5 mmol), 2.1 g of **4d** (48%) was isolated as yellow crystals (mp 207 °C). IR (Nujol): $\bar{\nu}$ 3292 (w) cm^{-1}, 3183 (m), 2213 (s), 1670 (s), 1593 (s), 1580 (s), 1497 (m). ^{1}H NMR (CD_2Cl_2): δ 1.32 (t, $J = 6.9$ Hz, 6 H, CH_2CH_3), 4.27 (m, $J = 6.9$ Hz, 4 H, CH_2CH_3), 6.97 (m, 4 H, Ph), 7.32 (m, 6 H, Ph), 11.38 (s, 2 H, NH). ^{13}C NMR (CD_2Cl_2): δ_C 14.2 (CH_2CH_3), 62.3 (CH_2CH_3), 77.8 (C, *C*CN), 115.8 (C, CN), 123.1, 127.9, 129.8 (CH, Ph), 136.2 (C, Ph), 157.4 (C, *C*NHPh), 167.5 (CO). MS (CI, H_2O) *m*/*z* (%): 431 (100) [$M^+ + 1$], 385 (10), 357 (16). Anal. Calcd for $C_{24}H_{22}N_4O_4$ (430.46): C, 66.97; H, 5.15; N, 13.02. Found: C, 67.17; H, 5.08; N, 13.07.

(*Z*,*Z*)-1,4-Dicyano-2,3-di(p-tolyl)aminobutadiene-1,4-dicarboxylic Acid Piperidide (4e). Starting with (cyanoacetyl)piperidine (0.76 g, 5 mmol) and **2a** (0.76 g, 2.5 mmol), 1.5 g of **4e** (56%) was isolated as a slightly yellow solid (mp 285−287 °C). IR (Nujol): $\bar{\nu}$ 3297 (s) cm^{-1}, 1678 (m). ^{1}H NMR (CD_2Cl_2): δ 1.28 (m, 12 H, CH_2), 2.39 (s, 6 H, Tol-CH_3), 2.70, 3.31, 3.74 (m, 20 H, NCH_2), 7.24 (m, 8 H, Tol), 8.36 (s, 2 H, NH). ^{13}C NMR (CD_2Cl_2): δ_C 21.2 (Tol-CH_3), 24.6, 25.5, 26.5, 42.8, 48.2 (CH_2), 96.5 (C, *C*CN), 126.5, 129.7 (CH, Tol), 137.9 (C, Tol-C to C), 145.2 (C, Tol-C to N), 161.7 (C, *C*NHTol), 165.8 (CO). MS (CI, H_2O) *m*/*z* (%): 537 (3) [$M^+ + 1$], 452 (8), 268 (3) [M^+/2], 147 (100). Anal. Calcd for $C_{32}H_{36}N_6O_2$ (536.68): C, 71.62; H, 6.76; N, 15.66. Found: C, 71.29; H, 6.88; N, 15.41.

(*Z*,*Z*)-1,4-Dicyano-2,3-di(*p*-tolyl)aminobutadiene-1,4-dicarboxylic Acid Morpholide (4f). Starting with (cyanoacetyl)morpholine (1.00 g, 6.48 mmol) and **2a** (0.99 g, 3.24 mmol), 1.26 g of **4f** (36%) was isolated as a slightly yellow solid (mp 307−308 °C). IR (Nujol): $\bar{\nu}$ 3475 (m) cm^{-1}, 3445 (s), 3276 (s), 1676 (w), 1635 (s), 1590 (s), 1579 (s), 1515 (m). ^{1}H NMR (DMSO-d_6): δ 2.34 (s, 6 H, Tol-CH_3), 3.28, 3.32 (m, 16 H, CH_2), 7.24 (m, 8 H, Tol), 8.73 (s, 2 H, NH). MS (CI, H_2O) *m*/*z* (%): 541 (12) [$M^+ + 1$], 454 (2), 88 (100). Anal. Calcd for $C_{30}H_{32}N_6O_4$ (540.62): C, 66.65; H, 5.97; N, 15.55. Found: C, 66.41. H, 6.05; N, 15.71.

Conversion of 4c and 4d into 5d and 5e, Respectively. A toluene solution (30 mL) of diketodienes **4c** or **4d** (0.5 g) was refluxed for 12 h. The solution became red after 6−8 h, and a red solid precipitated which was filtered, washed two times with hot toluene, and dried. The product was recrystallized from acetone to give 0.12 g (26%) of **5d** or 0.10 g (22%) of **5e**.

General Procedure for the Preparation of 5-Ylidenepyrrol-2(5*H*)-ones (5a−f). To a THF solution (20 mL) of diethyl malonate (0.88 mL, 8 mmol) or ethyl cyanoacetate (8 mmol) was added 14 mL of $NaN(SiMe_3)_2$ (1 M solution in THF) in 25 mL of THF. After 10 min of stirring at 0 °C, the suspension formed was transferred to a (green) THF solution (30 mL) of $CoBr_2$·2THF (0.72 g, 2 mmol) and the respective oxalic acid bis(imidoyl) dichloride (4 mmol) at −78 °C. After 12 h of stirring at 20 °C, the deep red solution was added to 250 mL of saturated aqueous solution of NH_4Cl. The organic layer was separated and dried (Na_2SO_4), and the solution was concentrated with a rotary evaporator. Purification was effected as indicated.

(*E*)-[1-(*p*-Tolyl)-3-[(*p*-tolyl)amino]-4-carboxyethyl-2-oxopyrrol-5-ylidene]dicarboxylic Acid Diethyl Ester (5a). Starting with diethyl malonate (8 mmol) and **2a** (1.22 g, 4 mmol), 556 mg of **5a** (54%) was isolated by column chromatography (silica gel, toluene/acetone = 10:1) as slightly yellow crystals (mp 128−130 °C). IR (Nujol): $\bar{\nu}$ 3264 (s) cm^{-1}, 1738 (s), 1711 (s), 1705 (s), 1635 (s). ^{1}H NMR (acetone-d_6): δ 0.97, 1.02, 1.19 (t, $J = 7.2$ Hz, 9 H, CH_2CH_3), 2.29, 2.32 (s, 6 H, Tol-CH_3), 3.38, 3.84, 4.08 (m, 6 H, CH_2CH_3), 7.05−7.25 (m, 8 H, Tol), 8.86 (s, 1 H, NH). ^{13}C NMR (acetone-d_6): δ_C 13.8, 13.9, 14.2 (CH_2CH_3), 20.9, 21.4 (Tol-CH_3), 61.4, 61.5, 61.6 (CH_2CH_3), 103.1 (C, C-6), 107.3 (C, C-4), 124.3, 126.0, 128.9, 129.1, 129.6, 129.9 (C, CH, Tol), 133.4 (C, C-3), 136.2, 138.9 (C, Tol-C to N), 149.4 (C, C-5), 164.4, 164.5, 165.3, 166.0 (C, C-2, CO). MS (EI) *m*/*z* (%): 506 (15) [M^+], 387 (67), 341 (100). Anal. Calcd for $C_{28}H_{30}N_2O_7$ (506.5): C, 66.39; H, 5.97; N, 5.53. Found: C, 66.32; H, 6.13; N, 5.67.

(*E*)-[1-(Phenyl)-3-(phenylamino)-4-(carboxyethyl)-2-oxopyrrol-5-ylidene]dicarboxylic Acid Diethyl Ester (5b). Starting with diethyl malonate (8 mmol) and **2b** (1.08 g, 4 mmol), 1.17 g of **5b** (61%) was isolated by column chromatog-

raphy (silica gel, toluene/acetone = 10:1) as slightly yellow crystals (mp 139−141 °C). IR (Nujol): $\bar{\nu}$ 3264 (s) cm^{-1}, 1738 (s), 1711 (s), 1705 (s), 1635 (s). ^1H NMR (CD_2Cl_2): δ 1.05, 1.20, 1.33 (t, J = 7 Hz, 9 H, CH_2CH_3), 3.68, 4.18 (m, 6 H, CH_2CH_3), 7.10−7.45 (m, 10 H, Ph), 8.58 (s, 1 H, NH). ^{13}C NMR (CD_2Cl_2): δ_C 13.9, 14.2, 14.8 (CH_2CH_3), 56.6, 58.7, 60.1 (CH_2CH_3), 94.4 (C, C-6), 103.1 (C, C-4), 123.6, 125.5, 127.3, 127.8, 129.0, 129.6 (CH, Ph), 135.3 (C, C-3), 139.3, 139.4 (C, Ph-C to N), 146.3 (C, C-5), 163.9, 164.6, 165.7, 166.2 (C, C-2, CO). MS (EI) *m*/*z* (%): 506 (15) [M^+], 387 (67), 341 (100). Anal. Calcd for $C_{28}H_{30}N_2O_7$ (506.5): C, 66.39; H, 5.97; N, 5.53. Found: C, 66.32; H, 6.13; N, 5.67.

(*E*)-[1-(*p*-Nitrophenyl)-3-[(*p*-nitrophenyl)amino]-4-(carboxyethyl)-2-oxopyrrol-5-ylidene]dicarboxylic Acid Diethyl Ester (5c). Starting with diethyl malonate (8 mmol) and *p*-bis[(*p*-nitrophenyl)imidoyl] chloride (1.47 g, 4 mmol), 1.27 g of **5c** (56%) was isolated by column chromatography (silica gel, toluene/acetone = 10:1) as slightly yellow crystals (mp 179−181 °C). IR (Nujol): $\bar{\nu}$ 3264 (s) cm^{-1}, 1738 (s), 1711 (s), 1705 (s), 1635 (s). ^1H NMR (CD_2Cl_2): δ 1.04, 1.21, 1.36 (t, J = 7 Hz, 9 H, CH_2CH_3), 3.70, 4.21 (m, 6 H, CH_2CH_3), 7.22 (m, 2 H, Ar), 7.70 (m, 2 H, Ar), 8.22 (m, 4 H, Ar), 8.84 (s, 1 H, NH). ^{13}C NMR (CD_2Cl_2): δ_C 13.9, 14.1, 14.3 (CH_2CH_3), 61.6, 62.0, 62.2 (CH_2CH_3), 94.7 (C, C-6), 108.4 (C, C-4), 122.6, 124.4, 124.7, 126.7 (CH, Ar), 141.3 (C, C-3), 144.5, 144.8, 144.9, 146.3 (C, Ar−C to N, C-5), 163.4, 164.0, 165.3, 165.9 (C, C-2, CO). MS (EI) *m*/*z* (%): 506 (15) [M^+], 387 (67), 341 (100). Anal. Calcd for $C_{28}H_{30}N_2O_7$ (506.5): C, 66.39; H, 5.97; N, 5.53. Found: C, 66.32; H, 6.13; N, 5.67.

(*E*)-[1-(*p*-Tolyl)-3-[(*p*-tolyl)amino]-4-cyano-2-oxopyrrol-5-ylidene]cyanoacetic Acid Ethyl Ester (5d). Starting with ethyl cyanoacetate (0.88 mL, 8 mmol) and **2a** (1.22 g, 4 mmol), 1.20 g of **5d** (71%) was isolated, by addition of a few drops of ether to 1 mL of a THF solution of the product, as slightly red crystals (mp 279 °C (dec)). IR (Nujol): $\bar{\nu}$ 3247 (s) cm^{-1}, 2220 (m), 2204 (m), 1737 (s), 1706 (s), 1641 (s). ^1H NMR (DMSO-d_6): δ 1.14 (t, 3 H, CH_2CH_3), 2.30, 2.33 (s, 6 H, Tol-CH_3), 4.15 (q, 2 H, CH_2CH_3), 7.35 (m, 8 H, Tol), 11.34 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6): δ_C 13.6 (CH_2CH_3), 20.9, 21.0 (Tol-CH_3), 61.7 (CH_2CH_3), 75.4 (C, C-6), 79.8 (C, C-4), 112.4, 120.3 (C, CN), 122.8, 124.3, 129.1, 129.6, 130.0, 130.1 (C, CH, Tol), 133.6 (C, C-3), 133.1, 136.8 (C, Tol-C to N), 146.6 (C, C-5), 158.0, 162.7 (C, C-2, CO). MS (EI) *m*/*z* (%): 412 (35) [M^+], 385 (17), 339 (100). Anal. Calcd for $C_{24}H_{20}N_4O_3$ (412.4): C, 69.89; H, 4.89; N, 13.58. Found: C, 70.18; H, 5.08; N, 13.44.

(*E*)-[1-Phenyl-3-(phenylamino)-4-cyano-2-oxopyrrol-5-ylidene]cyanoacetic Acid Ethyl Ester (5e). Starting with ethyl cyanoacetate (0.88 mL, 8 mmol) and **2b** (1.08 g, 4 mmol), 1.14 g of **5e** (74%) was isolated, by addition of a few drops of ether to 1 mL of a THF solution of the product, as slightly red crystals (mp 269−271 °C (dec)). IR (Nujol): $\bar{\nu}$ 3247 (s) cm^{-1}, 2220 (m), 2204 (m), 1737 (s), 1706 (s), 1641 (s). ^1H NMR (DMSO-d_6): δ 1.18 (br, 3 H, CH_2CH_3), 4.13 (br, 2 H, CH_2CH_3), 7.30−7.50 (m, 10 H, Ph), 11.44 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6): δ_C 13.6 (CH_2CH_3), 61.7 (CH_2CH_3), 75.8 (C, C-6), 79.9 (C, C-4), 111.4, 113.5 (C, CN), 124.5, 127.3, 128.6, 129.1 (CH, Ph), 132.5 (C, C-3), 135.7 (C, Ph-C to N), 146.8 (C, C-5), 161.8, 162.7 (C, C-2, CO). MS (EI) *m*/*z* (%): 412 (35) [M^+], 385 (17), 339 (100). Anal. Calcd for $C_{24}H_{20}N_4O_3$ (412.4): C, 69.89; H, 4.89; N, 13.58. Found: C, 70.18; H, 5.08; N, 13.44.

(*E*)-[1-(*p*-Methoxyphenyl)-3-[(*p*-methoxyphenyl)amino]-4-cyano-2-oxopyrrol-5-ylidene]cyanoacetic Acid Ethyl Ester (5f): Starting with ethyl cyanoacetate (0.88 mL, 8 mmol) and bis[(*p*-methoxyphenyl)imidoyl] chloride (1.35 g, 4 mmol), 1.17 g of **5f** (66%) was isolated, by addition of a few drops of ether to 1 mL of a THF solution of the product, as slightly red crystals (mp 256−258 °C (dec)). IR (Nujol): $\bar{\nu}$ 3247 (s) cm^{-1}, 2220 (m), 2204 (m), 1737 (s), 1706 (s), 1641 (s). ^1H NMR (DMSO-d_6): δ 1.16 (t, 3 H, CH_2CH_3), 3.77, 3.79 (s, 6 H, OCH_3), 4.00 (q, 2 H, CH_2CH_3), 7.00 (m, 4 H, Ar), 7.28 (m, 4 H, Ar), 11.31 (br, 1 H, NH). ^{13}C NMR (DMSO-d_6): δ_C 13.7 (CH_2CH_3), 55.3, 55.4 (OCH_3), 61.5 (CH_2CH_3), 74.6 (C, weak, C-6), 111.9 (C, CN), 113.8, 114.3, 125.9, 129.4, 130.2 (CH, C, Ar, C-3), 147.2 (C, C-5), 158.2, 159.9, 162.2, 162.8 (C, Ar−C to O, C-2, CO). MS (EI) *m*/*z* (%): 412 (35) [M^+], 385 (17), 339 (100). Anal. Calcd for $C_{24}H_{20}N_4O_3$ (412.4): C, 69.89; H, 4.89; N, 13.58. Found: C, 70.18; H, 5.08; N, 13.44.

General Procedure for the Hydrolysis of 5a,d. **5a** or **5d** was stirred for 10 min at 20 °C in an aqueous solution of KOH (30 mL, 1 M). The deep red solution was extracted with an aqueous solution of KOH (1 M) and with water. The aqueous layer was filtered, and the filtrate was neutralized by addition of hydrochloric acid (2 M solution). This precipitated the product which was filtered, washed (ether), and dried in vacuo.

(*E*)-[1-(*p*-Tolyl)-3-[(*p*-tolyl)amino]-4-(carboxyethyl)-2-oxopyrrol-5-ylidene]dicarboxylic Acid Anhydride (6a). Starting with **5a** (0.5 g, 1 mmol), 0.34 g (72%) of **6a** was isolated as slightly yellow crystals (mp 240 °C). IR (Nujol): $\bar{\nu}$ 3239 (m) cm^{-1}, 1734 (s), 1662 (s), 1636 (s). ^1H NMR (DMF-d_7): δ 1.04, 1.15 (t, J = 7 Hz, 6 H, CH_2CH_3), 2.30, 2.35 (s, 6 H, Tol-CH_3), 3.38 (q, J = 7 Hz, 4 H, CH_2CH_3), 7.10−7.30 (m, 8 H, Tol), 10.18 (s, 1 H, NH). ^{13}C NMR (DMF-d_7): δ_C 13.9 (CH_2CH_3), 20.7, 21.0 (Tol-CH_3), 65.8 (CH_2CH_3), 98.8 (C, C-6), 102.1 (C, C-4), 124.9, 125.0, 129.7, 130.0 (C, CH, Tol), 135.6 (C, C-3), 137.4, 139.5 (C, Tol-C to N), 151.8 (C, C-5), 160.1, 163.6, 165.9, 168.3 (C, C-2, CO). MS (EI) *m*/*z* (%): 478 (46) [M^+], 386 (100), 315 (14). Anal. Calcd for $C_{26}H_{26}N_2O_7$ (478.5): C, 65.26; H, 5.48; N, 5.85. Found: C, 65.52; H, 5.18; N, 5.71.

(*E*)-[1-(*p*-Tolyl)-3-[(*p*-tolyl)amino]-4-cyano-2-oxopyrrol-5-ylidene]cyanoacetic Acid (6b). Starting with **5d** (0.24 g, 0.58 mmol), 190 mg (70%) of **6b**·$2H_2O$ was isolated as slightly yellow crystals (mp 276−280 °C). IR (Nujol): $\bar{\nu}$ 3304 (m) cm^{-1}, 2230 (m), 2213 (m), 1722 (m), 1671 (s). ^1H NMR (DMF-d_7): δ 2.32, 2.33 (s, 6 H, Tol-CH_3), 4.12 (br, 4 H, H_2O), 7.30 (m, 8 H, Tol), 9.67 (s, 1 H, NH). ^{13}C NMR (DMF-d_7): δ_C 20.7 (Tol-CH_3), 81.3, 81.8 (C, C-6, C-4), 113.9, 114.6 (C, CN), 126.2, 128.6, 129.8, 134.5 (C, CH, Tol), 135.7, 137.1, 139.7 (C, C-3, Tol-C to N), 156.4 (C, C-5), 160.2, 161.8 (C, C-2, CO). MS (EI) *m*/*z* (%): 384 (7) [M^+], 340 (88), 44 (100). Anal. Calcd for $C_{22}H_{20}N_4O_5$ (420.4): C, 62.85; H, 4.79; N, 13.33. Found: C, 62.85; H, 4.62; N, 12.56.

Procedure for the Preparation of Cobalt Complex 2a-$CoBr_2$. $CoBr_2$·THF (1.29 g, 3.55 mmol) was suspended in 80 mL of diethyl ether, and 2.17 g (7.1 mmol) of $C_2Cl_2(NTol)_2$ was added. A red microcrystaline solid immediately precipitated which was filtered after 1 h of stirring at 0 °C giving 2.6 g of **2a-$CoBr_2$** (90%). IR (Nujol): $\bar{\nu}$ 1660 cm^{-1}. Anal. Calcd for $C_{32}H_{28}Br_2Cl_2N_4Co$ (829.17): Co, 7.1. Found: Co, 7.3.

Procedure for the Preparation of Nickel Complex 2a-$NiBr_2$. $NiBr_2$ (8.9 g, 40.7 mmol) was suspended in 100 mL of THF, and 13.6 g (44.8 mmol) of $C_2Cl_2(NTol)_2$ was added. The suspension was stirred for 3 d at 20 °C. The deep red crystals which precipitated were filtered giving 16.0 g of 2a-$CoBr_2$ (77%). IR (Nujol): $\bar{\nu}$ 1660 cm^{-1}, 1704, 1752. Anal. Calcd for $C_{24}H_{30}Br_2Cl_2N_2NiO_2$ (667.9): Ni, 9.2. Found: Ni, 9.5.

Procedure for the Conversion of 2a-$CoBr_2$ into 5d. To a THF solution (20 mL) of α-cyanoacetic acid ethyl ester (0.88 mL, 8 mmol) was added 14 mL of $NaN(SiMe_3)_2$ (1 M solution in THF) in 25 mL of THF. After 10 min of stirring at 0 °C, the suspension formed was transferred to a THF solution (30 mL) of **2a-$CoBr_2$** (2 mmol) at −78 °C. After 12 h stirring at 20 °C, the deep red solution was added to 250 mL of saturated aequous solution of NH_4Cl. The organic layer was separated and dried (Na_2SO_4), and the solution was concentrated using a rotary evaporator to give **5d** (85%) by addition of a few drops of ether to 1 mL of a THF solution of the crude product.

Preparation of Cobalt(II) Complex (7). $CoBr_2$·2THF (0.6 g, 1.66 mmol) and 1.52 g (3.31 mmol) of **4c** were dissolved in 50 mL of THF at 20 °C, and 3.31 mL of $NaN(SiMe_3)_2$ (1.0 M solution in THF) was added. The solution immediately changed to deep red, and the solution was stirred for 1 h. NaBr was removed by filtration (Celite), and the filtrate was concentrated in vacuo. Ether (50 mL) was added slowly which resulted in precipitation of cobalt(II) complex **7**·2THF as a deep red solid (1.55 g, 84%, referred to $CoBr_2$·2THF). IR (Nujol): $\bar{\nu}$ 3250 (m) cm^{-1}, 2208 (m), 2205 (m), 1738 (s), 1707 (s), 1667 (s), 1642 (s), 1608 (s), 1560 (s), 1538 (s), 1513 (s). MS (negative CI, H_2O) *m*/*z* (%): 973 [$M^+ - 1 - 2THF$] (1), 412 (100). Anal. Calcd for

$C_{60}H_{68}N_8O_{10}Co$ (1118.2): C, 64.45; H, 5.95; N, 10.02; Co, 5.27. Found: C, 63.95; H, 5.32; N, 10.47; Co, 4.99.

Hydrolysis of Cobalt(II) Complex (7). The complex **7** (0.41 g, 0.37 mmol) was dissolved in THF (25 mL), $Na[N(SiMe_3)_2]$ (1.10 mmol) in THF was added at −78 °C, and the solution was stirred for 1 h at 20 °C. The solution was poured into an aqueous solution (1.0 M) of NH_4Cl which was then extracted with THF/ether (1:1). The organic layers were combined, dried (Na_2SO_4), and filtered, and the solvent was removed in vacuo. To the residue was added ether (2 mL) which resulted in precipitation of a solid which was filtered and washed (ether), to give 0.27 g (87%) of **5d**.

Preparation of Cobalt(II) Complexes (9a,b). To a THF solution (20 mL) of ethyl cyanoacetate or diethyl malonate (8 mmol) was added 14 mL of $NaN(SiMe_3)_2$ (1 M solution in THF) in 25 mL of THF. After 10 min stirring at 0 °C, the suspension formed was transferred to a THF solution (30 mL) of $NiBr_2$·DME (2 mmol) and of the respective oxalic acid bis(imidoyl) dichloride (4 mmol) at −78 °C. After 12 h of stirring at 20 °C, the deep red solution was filtered (Celite) and the filtrate was concentrated in vacuo to ca. 10 mL without heating. Ether (20−30 mL) was added slowly which resulted in precipitation of metal complexes **9a,b** as deep red oils which solidified on standing for 3 d. The solids were filtered, washed with ether, and dried in vacuo.

Nickel(II) Complex (9a). Starting with $NiBr_2$·DME (0.42 g, 1.36 mmol), 0.73 g of **9a**·2THF (55%) was isolated. IR (Nujol): $\bar{\nu}$ 2200 (s) cm^{-1}, 1687 (s), 1612 (s), 1592 (s), 1520 (s). MS (negative CI, H_2O) *m*/*z* (%): 824 [$M^+ - 1 - 2THF$] (1), 519 (5), 412 (100). Anal. Calcd for $C_{52}H_{46}N_8O_8Ni$ (969.68): C, 64.41; H, 4.78; N, 11.56; Ni, 6.05. Found: C, 64.12; H, 4.93, N, 11.27.

Nickel(II) Complex (9b). Starting with $NiBr_2$·DME (0.16 g, 0.52 mmol), 0.24 g of **9b**·2THF (42%) was isolated. IR (Nujol): $\bar{\nu}$ 2198 (s) cm^{-1}, 1686 (s), 1609 (s), 1516 (s), 1502 (s). − MS (Negative CI, H_2O) *m*/*z* (%): 944 [$M^+ - 1 - 2THF$] (2), 519 (4), 444 (100).

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Supporting Information Available: Details of the complexation of **5d** with transition metals, of the AM1-calculations of isomers of **4c**, and of the structure determination for **4c**, **5a**, and **2a-NiBr$_2$** including atomic coordinates, H-atom coordinates, bond distances, and bond angles (23 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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