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Preparation and characterization of molybdenum and tungsten compounds with diazabutadiene ligands constructed from amino esters and glyoxal
Crystal structures of meso and C_2-symmetric isomers of $Mo(CO)_4$(dab-asp(OMe)-OMe)

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Abstract

The title compounds were prepared by heating solutions of ester protected amino acids (H-L-Ala-OEt, H-β-Ala-OEt, H-L-Val-OMe, GABA-OMe, H-L-Asp(OMe)-OMe) and glyoxal in the presence of $M(CO)_4(pip)_2$ (M = Mo, W). The resulting novel complexes, $M(CO)_4$(dab-xxx-OR) (dab = diazabutadiene), contain an *N,N′*-diimine ligand and were characterized by ^{1}H- and ^{13}C-NMR, IR, and UV–vis measurements. The low energy band in the visible portion of the electronic spectrum is assigned to a MLCT transition and exhibits solvatochromism. The valine, alanine and aspartic ester derivatives have C_2 symmetry resulting from the C_2 symmetry of the ligand. The reaction of the alanine and aspartic amino esters in the presence of NEt_3 produces diastereomeric mixtures caused by racemization at the amino acid α-carbon. Racemization is not observed during the formation of the valine derivatives. The crystal structures of (*R,S*)-$Mo(CO)_4$(dab-asp(OMe)-OMe) (**5-*RS***), and (*S,S*)-$Mo(CO)_4$(dab-asp(OMe)-OMe) (**5-*SS***), were determined. The structure of **5-*RS*** confirms that racemization at the α-carbon occurred. **5-*SS*** has C_2 symmetry.

Keywords: Diimine; Molybdenum; Tungsten; Amino acid; Crystal structures; Chiral ligand

1. Introduction

Organometallic compounds with diazabutadiene (dab) ligands have been extensively studied in recent years. While a number of different binding modes have been discovered [1], the most commonly observed mode is chelation of two imine nitrogens by one metal. This conjugated diimine structure often leads to stable compounds—especially in lower oxidation states where the strongly back-bonding characteristics of this ligand group can be utilized. Group 10 compounds with specially designed dab ligands containing a bulky side group have found practical uses as olefin polymerization catalysts [2–5].

Group 6 d^6 compounds of the general formula $M(CO)_4$(dab-R,R′), shown in Fig. 1, have received close scrutiny. While various diketones can be used for generation of the dab ligand, most work has been reported on the use of glyoxal (R′ = H) and 2,3-butanedione (R′ = Me) as the dicarbonyl source. A series of $Mo(CO)_4$(dab-R,R′) compounds, where R = alkyl, aryl, NH_2 or OH and R′ = Me, Ph, were first synthesized by tom Dieck and co-workers [6]. Preparation of the corresponding glyoxal derivatives (R′ = H) was realized shortly afterwards [7]. Interest in these systems stems from their stability, their interesting spectroscopic and photochemical properties, and the

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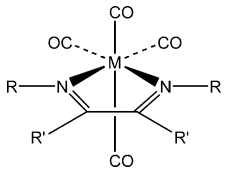

Fig. 1. Structure of $M(CO)_4$(dab-R,R′).

variety of related Group 6 compounds that can be made with this ligand set [6–14].

In this paper we report the preparation and characterization of novel molybdenum **1**–**5** and tungsten **6**–**10** derivatives that contain diazabutadiene ligands (dab-xxx-OR) prepared from condensation of ester protected amino acids with glyoxal. See Table 1 for the numbering scheme utilized. While the ligands cannot be isolated, the resulting organometallic compounds are stable. The spectroscopic properties of these new compounds are similar to diazabutadiene compounds reported previously but show the effects of electron withdrawing ester groups in the ligand.

Several of the compounds were prepared using chiral amino esters. This led to optically pure compounds containing a C_2-symmetric ligand for esters of alanine, valine and aspartic acid. When the syntheses were run in the presence of NEt_3, racemization at the α-carbon occurred leading to formation of a racemic mixture of diastereomers. The X-ray structures of the meso compound, (*R,S*)-Mo(dab-asp(Me)-OMe) (**5-*RS***), and the C_2-symmetric chiral diastereomer, (*S,S*)-Mo(dab-asp(Me)-OMe) (**5-*SS***), were determined to confirm the stereochemical assignments and the racemization process.

This work extends our previous study of $M(CO)_4$(N–N) (M = Cr, Mo, W) diimine compounds containing amino ester derivatized pyridinecarbaldehyde imine (pyca-xxx-OR) ligands formed from the condensation of pyridine-2-carboxaldehyde and one equivalent of an amino ester [15].

Table 1
Numbering scheme for $M(CO)_4$(dab-xxx-OR) compounds prepared

M = Mo	M = W	Amino ester, H_2N-xxx-OR	xxx-OR
1	**6**	H-L-Ala-OEt	$CHCH_3CO_2Et$
2	**7**	H-β-Ala-OEt	$CH_2CH_2CO_2Et$
3	**8**	H-L-Val-OMe	$CHCH(CH_3)_2CO_2Me$
4	**9**	GABA-OMe	$CH_2CH_2CH_2CO_2Me$
5	**10**	H-L-Asp(OMe)-OMe	$CHCH_2COOCH_3CO_2Me$

2. Results and discussion

2.1. Synthesis

Preparation of compounds **1**–**10** is most successful if the ligand is allowed to form for 20 min prior to addition of the metal precursor. The ligand cannot be isolated because it is not stable. Previous reports confirm that some diazabutadiene ligands are not stable and metal complexes can only be prepared via a one-pot reaction [1]. Addition of $M(CO)_4(pip)_2$ (M = Mo, W) to a solution of the ligand followed by reflux in methanol leads to deep blue or purple solutions indicative of formation of the product. The solutions rapidly darken when heated, but the reflux is maintained for 30 min to ensure completion of the reaction. Fig. 2 shows the general synthetic scheme used. Yields were maximized by using glyoxal and the amino ester in twice the required stoichiometric amounts.

Alternative synthetic methods were explored. Addition of NEt_3 to generate the neutral amino ester produced the meso and racemic diastereomers for the alanine and aspartic chiral amino esters. This was apparently caused by base-assisted proton removal at the α-carbon followed by re-protonation of the trigonal planar α-carbon. The relative amounts of diastereomers produced varied from one trial to the next. The diastereomers could not be separated by either crystallization or by silica gel column chromatography. Use of methylene chloride as solvent instead of methanol worked well only for the molybdenum derivatives but did not improve the yields of these compounds.

Chromatography led to a convenient separation of a deeply colored band from decomposition products and remaining starting material. The compounds, generated in varying yields, are air-stable as solids and slightly air-sensitive in solution. The aspartic ester derivatives were the most difficult to make and were obtained in the lowest yields, possibly due to the fact that the aspartic ester has the least basic amino group of the compounds studied because it has two electron withdrawing ester groups. Good elemental analysis results were obtained for all metal complexes reported.

2.2. Structure of (*R,S*)-Mo(CO)$_4$(dab-asp(OMe)-OMe), (**5-*SS***), and (*S,S*)-Mo(CO)$_4$(dab-asp(OMe)-OMe), (**5-*RS***)

The meso compound **5-*RS*** [16] was created along with the associated racemic mixture from the reaction between $Mo(CO)_4(pip)_2$, aspartic acid dimethyl ester hydrochloride, and glyoxal in the presence of NEt_3. The crystal was randomly chosen from the diastereomeric mixture of crystals grown in CH_2Cl_2–hexane following chromatography. The compound crystallizes in the space group $P\bar{1}$ with two identical molecules in each

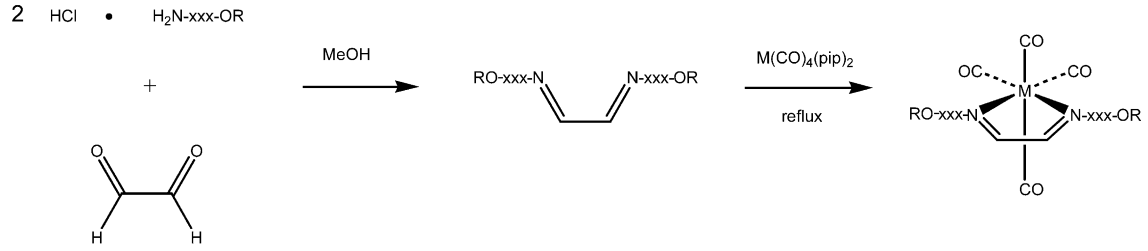

Fig. 2. General reaction scheme for the synthesis of compounds **1**–**10**.

unit cell. The molecular structure is illustrated in Fig. 3 along with the atom numbering scheme. Crystal data are given in Table 2 and relevant bond lengths and angles are found in Table 3.

Crystals of **5-*SS*** were grown in toluene following synthesis of this single diastereomer in the absence of NEt_3. The compound crystallizes in the chiral space group $P2_12_12_1$ with four identical structures in each unit cell. The molecular structure is illustrated in Fig. 4 along with the atom numbering scheme. Crystal data are given in Table 2 and relevant bond lengths and angles are found in Table 3.

Both compounds display a slightly distorted octahedral coordination geometry around Mo. This distortion is explained by the 72.31(8)° **5-*RS*** and 71.68(7)° **5-*SS*** bite angles measured for the bidentate diazabutadiene ligand, respectively. Their angles are similar to the value of 72.6(3)° measured for $W(CO)_3$(dab-*i*-Pr)(η^2-eco) (eco = (*E*)-cyclooctene) [17]. It is also similar to the value of 72.58(9)° observed for the pyridine carbaldehyde imine amino ester conjugate complex, $Mo(CO)_4$(pyca-β-ala-OEt) [15]. The ligand and metal in each structure are essentially co-planar consistent with the π-backbonding of this ligand. The N(1)–C(12), N(2)–C(11) and C(11)–C(12) bond distances of 1.293(3), 1.292(3) and 1.441(4) Å in **5-*RS*** and 1.288(3), 1.287(3) and 1.459(3) in **5-*SS***, respectively, confirm the conjugated diimine nature of this ligand [15,17]. Both structures have the aspartic ester

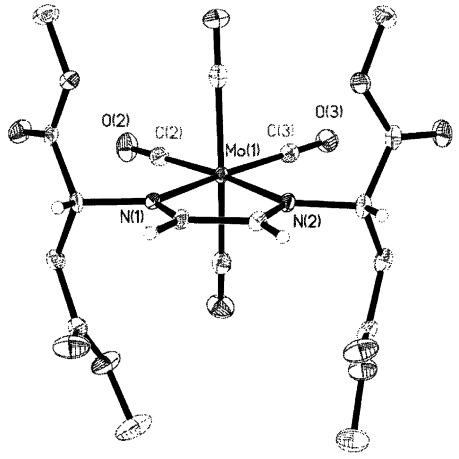

Fig. 3. Molecular structure (ORTEP drawing) for **5-*RS***.

Table 2
Crystal data and structure refinement for **5-*RS*** and **5-*SS***

Identification code	**5-*RS***	**5-*SS***
Empirical formula	$C_{18}H_{20}MoN_2O_{12}$	$C_{18}H_{20}MoN_2O_{12}$
Formula weight	552.30	552.30
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	10.0526(13)	11.032(5)
b (Å)	10.8251(14)	11.329(5)
c (Å)	11.9245(15)	18.668(8)
α (°)	109.084(2)	90
β (°)	102.832(2)	90
γ (°)	104.556(2)	90
V (Å^3)	1119.4(2)	2333.1(17)
Z	2	4
D_{calc} (g cm^{-3})	1.639	1.572
Absorption coefficient (mm^{-1})	0.652	0.626
F(000)	560	1120
Crystal size (mm^3)	0.35 × 0.10 × 0.05	0.40 × 0.40 × 0.30
θ Range for data collection (°)	2.13–28.26	2.10–28.30
Index ranges	$-13 \le h \le 13$, $-13 \le k \le 14$, $-15 \le l \le 15$	$-14 \le h \le 14$, $-14 \le k \le 15$, $-24 \le l \le 24$
Reflections collected	9650	19 133
Independent reflections	4989 [$R_{int} = 0.0265$]	5585 [$R_{int} = 0.0371$]
Completeness to θ = 28.26° (%)	90.0	98.2
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4989/0/366	5585/0/378
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0374$, $wR_2 = 0.0760$	$R_1 = 0.0262$, $wR_2 = 0.0625$
R indices (all data)	$R_1 = 0.0443$, $wR_2 = 0.0786$	$R_1 = 0.0271$, $wR_2 = 0.0650$
Goodness-of-fit on F^2	1.085	1.077
Largest difference peak and hole (e Å^{-3})	0.787 and −0.715	1.106 and −0.356

Table 3
Selected lengths (Å) and angles (°) for **5-*RS*** and **5-SS**

	5-*RS*	**5-*SS***
Bond lengths		
Mo(1)–C(3)	1.982(3)	1.966(2)
Mo(1)–C(2)	1.984(3)	1.965(3)
Mo(1)–C(4)	2.040(3)	2.058(3)
Mo(1)–C(1)	2.056(3)	2.030(3)
Mo(1)–N(1)	2.209(2)	2.252(2)
Mo(1)–N(2)	2.212(2)	2.258(2)
N(1)–C(12)	1.293(3)	1.288(3)
N(1)–C(15)	1.480(3)	
N(2)–C(11)	1.292(3)	1.287(3)
N(2)–C(7)	1.475(3)	1.483(3)
C(11)–C(12)	1.441(4)	1.459(3)
Bond angles		
C(3)–Mo(1)–C(2)	89.49(11)	84.92(9)
C(3)–Mo(1)–C(4)	86.02(11)	84.96(10)
C(2)–Mo(1)–C(4)	86.23(11)	85.07(10)
C(3)–Mo(1)–C(1)	86.69(11)	85.87(10)
C(2)–Mo(1)–C(1)	83.29(11)	87.58(10)
C(4)–Mo(1)–C(1)	167.28(11)	168.71(10)
C(3)–Mo(1)–N(1)	169.55(10)	173.07(8)
C(2)–Mo(1)–N(1)	100.76(10)	101.24(8)
C(4)–Mo(1)–N(1)	92.57(9)	92.35(9)
C(1)–Mo(1)–N(1)	96.44(9)	97.49(9)
C(3)–Mo(1)–N(2)	97.48(10)	102.14(8)
C(2)–Mo(1)–N(2)	172.94(10)	172.92(8)
C(4)–Mo(1)–N(2)	95.28(10)	94.89(9)
C(1)–Mo(1)–N(2)	95.99(10)	93.47(9)
N(1)–Mo(1)–N(2)	72.31(8)	71.68(7)
N(2)–C(11)–C(12)	116.7(2)	117.4(2)
N(1)–C(12)–C(11)	117.0(2)	117.2(2)

residues lying in an extended fashion that aligns them co-linear to the pair of trans COs. Furthermore, in each structure the C_α–H bond is co-planar to the diazabutadiene with the hydrogen lying proximal to the diazabutadiene. For **5-*RS*** this means that the methylene groups of the aspartic ester residue are in a cis position leading to the C_s symmetry observed in Fig. 5. For **5-*SS*** the molecular structure has the two methylenes trans to one another in a C_2-symmetrical arrangement. The molecular structure of **5-*RS*** shows definitively that one amino ester has racemized from *S* to *R* stereochemistry (the aspartic residue on the right at the top of Fig. 5). Conversely **5-*SS*** shows that both residues have maintained their stereochemistry at the α-carbon during the synthesis.

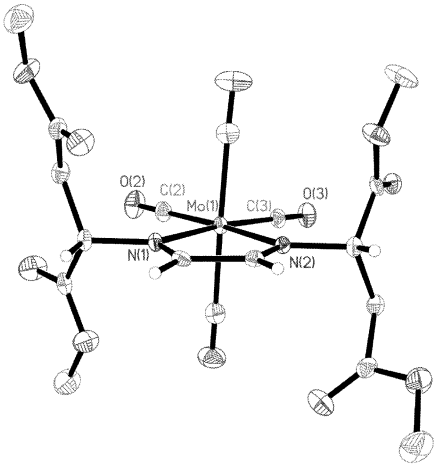

Fig. 4. Molecular structure (ORTEP drawing) for **5-*SS***.

2.3. Spectroscopic properties

Infrared spectra of the compounds show four bonds due to metal carbonyls stretches in a pattern consistent with compounds having a *cis*-$M(CO)_4L_2$ geometry [18]. An additional band, or in some cases two bands, at around 1735 cm^{-1} are observed for the ester carbonyl stretches.

^1H- and ^{13}C-NMR spectra are reported for all derivatives (Tables 4 and 5). In both the ^1H and ^{13}C spectra, one peak (with splitting as appropriate in the ^1H spectrum) is observed for the imine and the ester portions of the molecule. The resonances occur in the region of the spectrum expected in each case. The simplicity of the spectra (e.g. single imine peak in both the ^1H- and ^{13}C-NMR spectra) of compounds **2**, **4**, **7** and **9** which contain an amino ester without a stereocenter underscores the expected C_2 or C_s symmetry (depending on the orientation of the amino ester) for these compounds. The preparation of **1**, **5**, **6**, **10** as optically pure compounds (i.e. **1-*SS***, **5-*SS***, **6-*SS*** and **10-*SS***) leads to similarly simple spectra due to the C_2 symmetry imposed on the compound by the C_2-symmetric ligand. Performing the syntheses of **1**, **5**, **6**, and **10** in the presence of NEt_3 leads to isolation of mixtures of the meso and racemic compounds (e.g. **1-*RS***, **1-*RR*** and **1-*SS***). The NMR spectra of these mixtures are consequently more complicated with several peaks in each spectrum mirrored with a nearby peak of lesser intensity but with the same multiplicity (Tables 4 and 5). Comparison with the spectra of the optically pure compound permits identification of peaks produced by the meso compounds. Surprisingly, only one set of peaks is seen in the ^1H- and ^{13}C-NMR spectra of the valine derivatives (**3** and **8**) when NEt_3 is present during the synthesis. The reason racemization is not observed is not known.

2.4. Electronic spectroscopy

The compounds each show a symmetric, low energy band whose λ_{max} lies between 521 and 573 nm with an extinction coefficient of between and 7600 and 16,000 M^{-1} cm^{-1} (Table 6). This band has been previously ascribed to a combination of MLCT transitions for group 6 $M(CO)_4$(dab-*i*-Pr) complexes [19–23]. The transition shows the expected negative solvatochromism. The shift in λ_{max} is less than observed for the

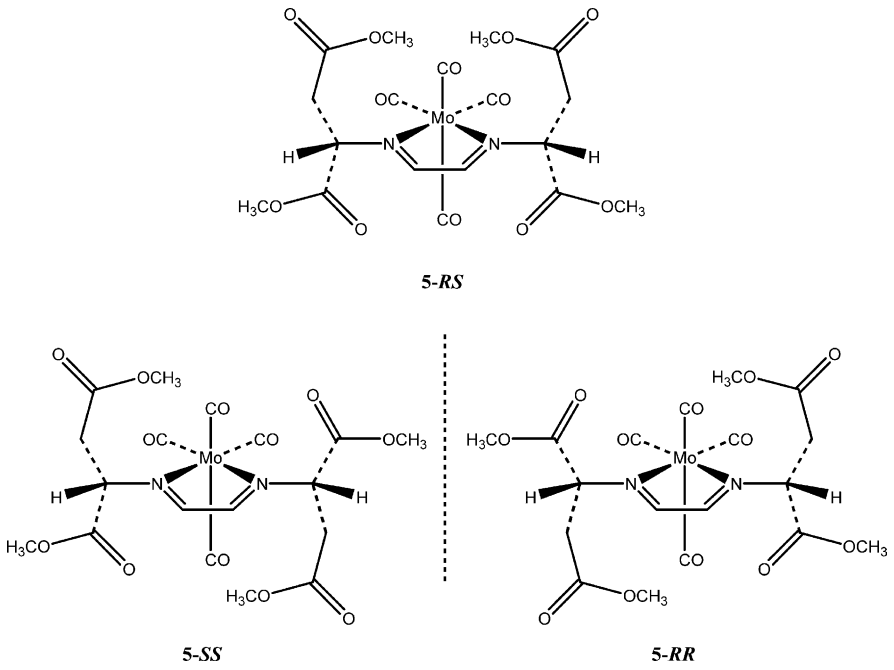

Fig. 5. Diastereomers for **5**: **5-*RS*** is the meso compound; **5-*RR*** and **5-*SS*** are C_2 symmetric.

corresponding pyridine aldehyde imine amino ester compounds [15]. The lesser solvatochromism for diazabutadiene complexes compared to pyridine carbaldehyde imine or bipyridine and phenanthroline derivatives has been observed previously and is attributed to a greater mixing of the d_π and π^* orbitals for diazabutadiene systems [19,20,22]. The effect of the ester group on the energy of the transition is clearly shown by its separation from the imine. Compounds **2**, **4**, **7**, and **9** each have the ester separated from the imine by two or three methylene groups. The MLCT bands for these compounds each lie about 30 nm to higher energy than the remaining compounds in which the esters are separated from the imine by one methylene group. Each compound studied also shows a solvent insensitive band between 360 and 373 nm that has an extinction coefficient of about 1500 M^{-1} cm^{-1}. This has been previously assigned to a d–d transition for related

Table 4
^{13}C-NMR for reported compounds [a]

Compounds	CO [b]	C=N	α-C	β-C	OCO	Other
1-*SS*	-	158.7	71.4	19.7	169.7	62.3 CH_2, 19.7 $CHCH_3$, 14.0 CH_2CH_3
1-*RS* [c]	-	158.7	71.4	19.6	169.7	62.3 CH_2, 19.6 $CHCH_3$, 14.0 CH_2CH_3
2	-	160.4	- [d]	35.6	171.1	61.3 CH_2, 60.9 CH_2, 14.1 CH_3
3	-	158.6	82.2	31.5	169.6	52.3 CH_3, 19.2 $CH(CH_3)_2$, 18.8 $CH(CH_3)_2$
4	-	158.7	65.1	- [d]	173.0	51.8 CH_3, 30.6 CH_2, 27.1 CH_2
5-*SS*	-	162.3	72.7	37.6	170.8, 168.2	53.2 $COOCH_3$, 52.1 $COOCH_3$
5-*RS* [c]	-	162.4	72.8	37.5	170.6, 168.0	53.2 $COOCH_3$, 52.2 $COOCH_3$
6-*SS*	207.0 [e]	159.2	72.0	20.4	170.1	62.3 CH_2, 19.7 $CHCH_3$, 14.0 CH_2CH_3
6-*RS* [c]	206.9	159.3	72.0	20.3	170.0	62.3 CH_2, 19.6 $CHCH_3$, 14.0 CH_2CH_3
7	207.5	161.8	- [d]	37.0	171.3	62.5 CH_2, 61,1 CH_2, 14.3 CH_3
8	207.1 [f]	158.8	88.8	32.6	170.5	52.6 CH_3, 19.6 $CH(CH_3)_2$, 18.9 $CH(CH_3)_2$
9	208.1	160.2	66.2	- [d]	173.3	52.1 CH_3, 30.9 CH_2, 28.4 CH_2
10-*SS*	205.6	163.1	73.6	38.7	170.7, 168.2	53.2 $COOCH_3$, 52.2 $COOCH_3$
10-*RS* [c]	205.6	163.0	73.7	38.6	170.6, 168.2	53.2 $COOCH_3$, 52.1 $COOCH_3$

[a] Recorded in $CDCl_3$. See Fig. 2 for general structure.
[b] Metal carbonyl resonances for molybdenum compounds were not observed. One metal carbonyl resonance was observed for tungsten compounds.
[c] Some peaks overlap in spectra of diasteromeric mixtures.
[d] CH_2 groups could not be distinguished.
[e] $J_{C-W} = 142$ Hz.
[f] $J_{C-W} = 143$ Hz.

Table 5
^{1}H-NMR [a] for reported compounds

Compounds	H–C=N	α-C–H	Other
1-*SS*	8.39	4.87 q (6.8)	4.27 m CH_2, 1.80 d (6.8) CHCH_3, 1.33 t (7.0) CH_2CH_3
1-*RS* [b]	8.39	4.87 q (6.8)	4.27 m CH_2, 1.86 d (6.8) CHCH_3, 1.33 t (7.0) CH_2CH_3
2	8.29	4.32 t (6.2)	4.11 q (7.2) CH_2CH$_3$, 3.12 t (6.0) CH_2C=O, 1.23 t (7.0) CH_3
3	8.45	4.42 d (10.0)	3.81 s CH_3, 2.64 m CH(CH$_3$)$_2$, 1.10 d (6.4) CH(CH_3)$_2$, 0.91 d (6.4) CH(CH_3)$_2$
4	8.17	4.13 t (6.6)	3.71 s CH_3, 2.36 m CH_2CH_2C=O
5-*SS*	8.46	5.10 dd (9.2, 8.8)	3.82 s CH_3, 3.68 s CH_3, 3.46 m CH_2
5-*RS* [b]	8.45	5.10 dd (9.2, 4.9)	3.84 s CH_3, 3.66 s CH_3, 3.46 m CH_2
6-*SS*	8.74	5.02 q (6.8)	4.29 m CH_2, 1.82 d (7.0) CHCH_3, 1.33 t (7.4) CH_2CH_3
6-*RS* [b]	8.74	5.02 q (6.8)	4.29 m CH_2, 1.81 d (7.0) CHCH_3, 1.33 t (7.4) CH_2CH_3
7	8.61	4.41 t (8.3)	4.11 m CH_2CH$_3$, 3.11 t (6.2) CH_2C=O, 1.21 t (7.0) CH_3
8	8.84	4.61 d (10.3)	3.81 s CH_3, 2.61 m CH(CH$_3$)$_2$, 1.09 d (6.4) CH(CH_3)$_2$, 0.91 d (6.3) CH(CH_3)$_2$
9	8.49	4.23 t (6.8)	3.71 s CH_3, 2.36 m CH_2CH_2C=O
10-*SS*	8.80	5.23 dd (8.8, 8.4)	3.82 CH_3, 3.68 CH_3, 3.49 m CH_2
10-*RS* [b]	8.81	5.23 dd (8.6, 7.6)	3.85 CH_3, 3.66 CH_3, 3.49 m CH_2

[a] Recorded in $CDCl_3$. See Fig. 2 for general structure.
[b] Some peaks overlap in spectra of diasteromeric mixtures.

diazabutadiene compounds based on the solvent insensitivity and the lower intensity [18,23].

3. Experimental

3.1. Spectroscopic measurements

NMR spectra were recorded on Varian 400 MHz UNITYINOVA and Bruker AC-300 spectrometers. Infrared spectra were recorded on 150 Nicolet and Perkin–Elmer 1750 FTIR spectrometers and electronic spectra were obtained with a Hitachi U-2000 spectrometer. Elemental Analysis were performed by Atlantic Microlab of Norcross, GA 30091.

3.2. Materials

Starting materials were obtained from commercial sources and were used without further purification. All solvents were degassed prior to use. A nitrogen atmosphere was used for all syntheses. $M(CO)_4(pip)_2$ (M = Mo, W; pip = piperidine) was prepared in standard fashion [24].

Table 6
Electronic spectra for compounds **1**–**10** in toluene and methanol.

Compounds	Toluene [a]	Methanol [a]	Δ [b]
1	568 (7.6)	555 (5.9)	412
2	537 (13)	522 (8.5)	535
3	573 (16)	557 (9.6)	501
4	539 (12)	522 (9.2)	604
5	573 (10)	556 (8.5)	533
6	554 (13)	544 (10)	331
7	533 (10)	522 (13)	395
8	554 (10)	549 (12)	164
9	532 (13)	521 (8.6)	397
10	562 (15)	550 (11)	388

[a] λ_{max}, nm (ε, $\times 10^{-3}$ M^{-1} cm^{-1}).
[b] Difference in cm^{-1} between MLCT band in methanol and toluene.

3.3. Synthesis of *1*–*10*

In a typical reaction glyoxal (40% by weight, 2.11 mmol) and the amino acid, H-xxx-OR·HCl (4.22 mmol), were added to a Schlenk flask containing methanol. The solution was degassed with nitrogen then stirred for 20 min. $Mo(CO)_4(pip)_2$ or $W(CO)_4(pip)_2$ (1.06 mmol) was added and the solution brought to reflux. After 30 min the solvent was removed. The compound was flash chromatographed with ethyl acetate–hexane mixed solvents on a silica gel column. The intensely colored band that eluted was isolated and solvent removed. The product was recrystallized yielding dark purple or black crystals. Synthesis of diastereomeric mixtures of **1**, **5**, **6** and **10** were carried out in a similar manner except twice the stoichiometric amount of NEt_3 was added before reflux was initiated.

Compound **1**: 30% yield. IR (CH_2Cl_2): 2023(s), 1927(vs), 1908(sh), 1856(s), 1734(m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{20}MoN_2O_8$: C, 41.39; H, 4.34; N, 6.03. Found: C, 41.17; H, 4.38; N, 6.22%.

Compound **2**: 61% yield. IR (CH_2Cl_2): 2021(s), 1922(vs), 1902(sh), 1851(s), 1732(m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{20}MoN_2O_8$: C, 41.39; H, 4.34; N, 6.03. Found: C, 41.57; H, 4.34; N, 6.19%.

Compound **3**: 72% yield. IR (CH_2Cl_2): 2021(s), 1925(vs), 1910(sh), 1862(s), 1749(sh, ester), 1734(m, ester) cm^{-1}. Anal. Calc. for $C_{18}H_{24}MoN_2O_8$: C, 43.91; H, 4.91; N, 5.69. Found: C, 43.98; H, 4.89; N, 5.77%.

Compound **4**: 40% yield. IR (CH_2Cl_2): 2018(s), 1920(vs), 1905(sh), 1854(s), 1734(m, ester) cm^{-1}. Anal.

Calc. for $C_{16}H_{20}MoN_2O_8$: C, 41.39; H, 4.34; N, 6.03. Found: C, 41.39; H, 4.30; N, 6.13%.

Compound **5**: 30% yield. IR (CH_2Cl_2): 2025(s), 1931(vs), 1913(sh), 1860(s), 1736(m, ester) cm^{-1}. Anal. Calc. for $C_{18}H_{20}MoN_2O_{12}$: C, 39.14; H, 3.65; N, 5.07. Found: C, 39.20; H, 3.62; N, 5.11%.

Compound **6**: 22% yield. IR (CH_2Cl_2): 2013(s), 1922(vs), 1907(sh), 1859(s), 1737(m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{20}N_2O_8W$: C, 34.80; H, 3.65; N, 5.07. Found: C, 34.80; H, 3.76; N, 5.30%.

Compound **7**: 35% yield. IR (CH_2Cl_2): 2017(s), 1917(vs), 1895(sh), 1854(s), 1733(m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{20}N_2O_8W$: C, 34.80; H, 3.65; N, 5.07. Found: C, 34.36; H, 3.79; N, 5.10%.

Compound **8**: 92% yield. IR (CH_2Cl_2): 2018(s), 1920(vs), 1903(sh), 1862(s), 1739(m, ester) cm^{-1}. Anal. Calc. for $C_{18}H_{24}N_2O_8W$: C, 37.26; H, 4.17; N, 4.83. Found: C, 37.48; H, 4.28; N, 4.88%.

Compound **9**: 38% yield. IR (CH_2Cl_2): 2015(s), 1914(vs), 1905(sh), 1854(s), 1734(m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{20}N_2O_8W$: C, 34.80; H, 3.65; N, 5.07. Found: C, 34.70; H, 3.42; N, 5.01%.

Compound **10**: 14% yield. IR (CH_2Cl_2): 2020(s), 1923(vs), 1908 (sh), 1861(s), 1739(m, ester) cm^{-1}. Anal. Calc. for $C_{18}H_{20}N_2O_{12}W$: C, 33.77; H, 3.15; N, 4.38. Found: C, 34.02; H, 3.25; N, 4.40%.

3.4. X-ray structure determination of 5-*RS* and 5-*SS*

Purple crystals of **5-*RS*** were obtained by slow diffusion of hexane into a CH_2Cl_2 solution containing the compound. Purple crystals of **5-*SS*** were grown from a slowly cooled toluene solution. Crystals were mounted on a cryoloop using Paratone N-Exxon oil and placed under a stream of nitrogen. Analyses of the data sets showed negligible decay during data collection. The data were corrected for absorption with the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.1), and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of F^2 converged [25]. Additional experimental details are provided in Table 2.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 215988 and 215987 for compounds **5-*RS*** and **5-*SS***. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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