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Preparation and characterization of rhenium(I) compounds with amino ester derivatized diimine ligands. Investigations of luminescence. Crystal structures of $Re(CO)_3Cl$(pyca-β-Ala-OEt) and $Re(CO)_3Cl$(pyca-L-Asp(OMe)-OMe)

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Abstract

The title compounds were prepared in good yield by heating ester protected amino acids (H-L-Ala-OEt, H-β-Ala-OEt, H-L-Val-OMe, H-GABA-OMe, H-L-Asp(OMe)-OMe, H-L-Met-OMe) with $Re(CO)_5Cl$ in the presence of pyridine-2-carboxaldehyde. The resulting novel complexes contain a bound, conjugated diimine ligand with a pendant ester group. All compounds were characterized by ^1H and ^{13}C NMR, IR and UV–Vis spectroscopy. Compounds prepared from chiral amino esters give diastereomers because of the presence of a stereogenic metal center. Syntheses using $Re(CO)_5Br$ as starting material were discontinued because of metathesis involving the chloride in the amino ester · HCl salts and the metal bromide. Photophysical studies on $Re(CO)_3Cl$(pyca-β-Ala-OEt), **2**, show that it is luminescent in organic solvents in air at room temperature. The crystal structures of **2** and $Re(CO)_3Cl$(pyca-L-Asp(OMe)-OMe), **5**, were determined.

Keywords: Rhenium; Diimine; Amino acid; Crystal structures; Luminescence

1. Introduction

Recent years have seen a surge of activity aimed at attaching biological molecules to organometallic reaction centers for medical purposes, prompting leading investigators to refer to the new field as bioorganometallic chemistry [1]. Various biological classes of compounds have been examined including steroids [2,3], sugars [4,5], nucleobases [6,7], and receptor molecules [8]. The diverse properties available to organometallic compounds, including paramagnetism [9], the infrared spectra of metal carbonyls [10], photoinduced electron transfer [11], and γ-emission [12] or β-emission [13] from radioactive nuclei, provide hope that novel bioconjugates could be used as biomarkers or for therapeutic purposes.

A common goal is to find robust compounds that can withstand harsh biological conditions – an environment foreign to much of organometallic chemistry. In recent years, work has shown that attaching the $[M(CO)_3]^+$ core (M = Re, Tc) [13,14] to biological compounds creates bioconjugates that show varying degrees of resistance to decomposition by air, water and biological conditions. A host of $[M(CO)_3]^+$ bound tridentate ligands [15–19] adapted to bind biological molecules, including neuropeptides [20–22], have been reported based on this core. Various compounds containing

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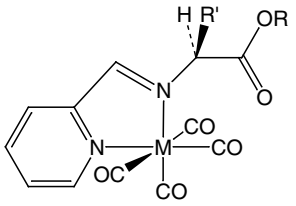

Fig. 1. Structure of $M(CO)_4$(pyca-Xxx-OR); M = Cr, Mo,W.

multidentate ligands have been tested and it has been discovered that N-heterocyles form especially strong bonds to Re(I) metal centers [18].

Amino acid and peptide attachments have been especially closely studied [23]. A common obstacle is that the hard base character of the amino and carboxylate ends of the amino acid renders them weakly binding ligands for organometallic centers. We chose to circumvent this obstacle by incorporating the amino acid in a strongly binding conjugated diimine ligand. The first report of this chemistry focused on $M(CO)_4$(pyca-Xxx-OR) compounds (M = Cr, Mo, W; pyca = pyridine-2-carbaldehyde imine; Xxx identifies the amino acid) shown in Fig. 1 [24].

We recently extended this work to the corresponding diazabutadiene ligands containing amino ester fragments [25]. It was found that employing NEt_3 to remove HCl from the amino ester during the synthesis leads to racemization of the α-carbon. Crystal structures of two diastereomers of $Mo(CO)_4$(dab-Asp(OMe)-OMe) confirmed this point.

This paper reports the first results of extending this stable diimine ligand system to rhenium. A principal driving force for this work was that d^6 diimine carbonyl systems often exhibit unusual air stability for organometallic systems. In addition, we were interested in seeing if luminescent amino acid conjugates could be prepared since this could be a sensitive technique for labeling biological systems. We report here the preparation and characterization of novel Re(I) compounds **1**–**6** that contain pyridinecarbaldehyde imine (pyca-Xxx-OR) ligands (see Table 1 for the numbering scheme used for these compounds). The compounds were readily prepared in good yield and were spectroscopically characterized. Preliminary studies on $Re(CO)_3Cl$(pyca-β-Ala-OEt), **2**, show that it is luminescent in air at room temperature. Also included are the x-ray structural characterizations of **2** and $Re(CO)_3Cl$(pyca-L-Asp(OMe)-OMe), **5**.

Table 1
Numbering scheme for derivatives of $Re(CO)_3Cl$(pyca-Xxx-OR)

Compound	Amino ester	–Xxx–	R
1	H-L-Ala-OEt	$–CH(CH_3)CO–$	Et
2	H-β-Ala-OEt	$–CH_2CH_2CO–$	Et
3	H-L-Val-OMe	–CH(i-Pr)CO–	Me
4	H_2N-$(CH_2)_3$-CO_2Me[a]	$–CH_2CH_2CH_2CO–$	Me
5	H-L-Asp(OMe)-OMe	$–CH(CH_2COOCH_3)CO–$	Me
6	H-L-Met-OMe	$–CH(CH_2CH_2SCH_3)CO–$	Me

[a] GABA is γ-aminobutyric acid.

2. Results and discussion

2.1. Synthesis

Pyridine-2-carboxaldehyde and the appropriate amino ester hydrochloride salt were stirred in methanol under nitrogen at room temperature for 20 min. Addition of $Re(CO)_5Cl$ and reflux for one hour produced the product (Fig. 2). The products are the amino acid conjugate complexes **1**–**6**. They were easily purified giving air-stable, bright orange, crystalline compounds in 47–86% yield. Initial attempts at synthesis were employed using readily prepared $Re(CO)_5Br$. It was found that the bromide ligand undergoes partial metathesis with the chloride from the amino acid ester hydrochloride salts in refluxing methanol. $Re(CO)_5Br$ was abandoned as a reagent in favor of $Re(CO)_5Cl$ ending the problem.

The syntheses were performed without added base because previously [25] we found that NEt_3 promotes inversion at the amino ester α-carbon. Good yields were obtained for the compounds when prepared without NEt_3, presumably because attachment of the diimine to the metal drives the equilibrium between the diimine and the aldehyde and amine to the right. Also, it was recently reported that condensation reactions between amines and pyridine aldehydes or pyridine ketones were accelerated by the presence of $Re(CO)_5Cl$. This acceleration occurs because the aldehyde or ketone is bound as a bidentate ligand (bound through the pyridine nitrogen and the carbonyl oxygen), which is rapidly attacked by primary amines yielding the diimine [26].

Because the metal center is a stereogenic center (pseudo-tetrahedral geometry if the three facial carbonyls are considered one unit), we were alert to the possibility of diastereomers for compounds prepared using chiral amino esters. NMR analysis (discussed below) confirmed

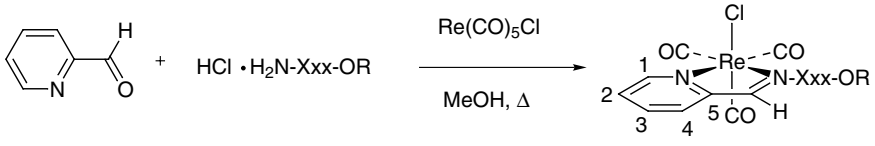

Fig. 2. General reaction scheme for synthesis of compounds **1**–**6** along with the labeling scheme for NMR identification.

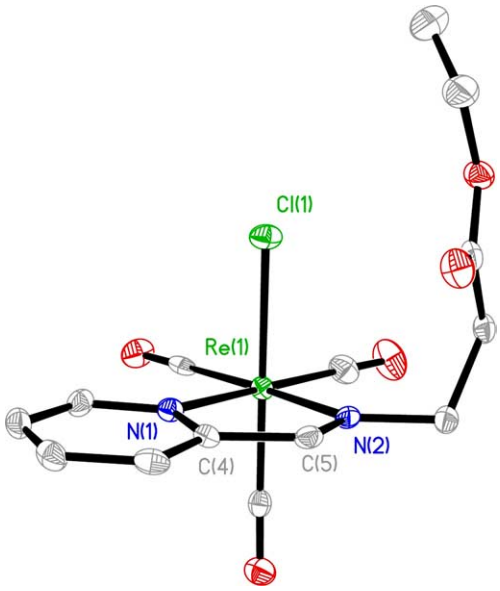

Fig. 3. Molecular structure with 30% thermal ellipsoids for **2**.

that **1**, **3**, **4** and **6** were formed as diastereomers. Attempts to separate them by chromatography and fractional crystallization were unsuccessful.

2.2. Crystal structures of $Re(CO)_3Cl$(pyca- β-Ala-OEt), **2** and $Re(CO)_3Cl$(pyca-L-Asp(OMe)-OMe), **5**

Crystals of **2** were grown by layering hexanes over a solution of CH_2Cl_2 containing the compound and allowing the layers to slowly mix. The compound crystallizes in the space group $P2_1/n$ with one molecule in the asymmetric unit. The molecular structure is illustrated in Fig. 3. Crystal data are given in Table 2 and relevant bond lengths and angles are found in Table 3.

Crystals of **5** were grown by slow evaporation of a solution of **5** dissolved in ethyl acetate and hexane. The compound crystallizes in the space group $P2_1$ with one molecule in the asymmetric unit. The molecular structure is illustrated in Fig. 4. 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 structure caused by the 74.8(1)° (**2**) and 75.3(3)° (**5**) bite angles for the diimine ligands in the two compounds. The pyridine and imine portions of the pyca ligand are essentially coplanar with the metal atom also lying in the plane. This is consistent with the strong π-backbonding expected for this ligand system. The

Table 2
Crystal data and structure refinement for **2** and **5**

Identification code	**2**	**5**
Empirical formula	$C_{14}H_{14}ClN_2O_5Re$	$C_{15}H_{14}ClN_2O_7Re$
Formula weight	511.92	555.93
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*n*	*P*2(1)
Unit cell dimensions		
a (Å)	14.8073(15)	11.217(3)
b (Å)	6.7752(7)	7.0174(16)
c (Å)	17.5915(18)	11.721(3)
α (°)	90	90
β (°)	108.097(2)	105.450(4)
γ (°)	90	90
Volume (Å^3)	1677.5(3)	889.2(3)
Z	4	2
Density (calculated) (Mg/m^3)	2.027	2.076
Absorption coefficient (mm^{-1})	7.428	7.023
F(0 0 0)	976	532
Crystal size (mm^3)	0.40 × 0.20 × 0.10	0.50 × 0.20 × 0.10
θ range for data collection (°)	1.58–28.28	1.88–26.00
Index ranges	$-19 \leqslant h \leqslant 19$, $-8 \leqslant k \leqslant 9$, $-22 \leqslant l \leqslant 23$	$-13 \leqslant h \leqslant 13$, $-8 \leqslant k \leqslant 8$, $-14 \leqslant l \leqslant 14$
	14,250	6748
	4028 [R_{int} = 0.0389]	3385 [R_{int} = 0.0450]
Completeness to θ	96.8% (θ = 28.28°)	99.7% (θ = 26.00°)
Absorption correction	SADABS	SADABS
Maximum and minimum transmission	0.5238 and 0.1551	0.5402 and 0.1271
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4028/0/264	3385/1/238
Goodness-of-fit on F^2	1.068	1.038
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0246, wR_2 = 0.0549	R_1 = 0.0410, wR_2 = 0.0926
R indices (all data)	R_1 = 0.0280, wR_2 = 0.0563	R_1 = 0.0449, wR_2 = 0.0938
Largest difference peak and hole (e Å^{-3})	1.172 and −0.864	3.271 and −2.093
Flack parameter		0.073(17)

Table 3
Selected bond lengths (Å) and bond angles (°) for **2** and **5**

	2	**5**
Bond lengths		
Re(1)–C(2)	1.917(4)	1.897(10)
Re(1)–C(3)	1.924(4)	1.951(12)
Re(1)–C(1)	1.910(4)	1.992(11)
Re(1)–N(1)	2.176(3)	2.170(9)
Re(1)–N(2)	2.178(3)	2.187(7)
Re(1)–Cl(1)	2.4825(8)	2.456(3)
N(2)–C(9)	1.274(4)	1.262(13)
N(1)–C(8)	1.354(4)	1.377(13)
C(9)–C(8)	1.461(5)	1.440(15)
Bond angles		
C(2)–Re(1)–C(3)	87.85(15)	90.3(4)
C(2)–Re(1)–C(1)	89.04(15)	90.2(4)
C(3)–Re(1)–C(1)	89.09(14)	89.7(4)
C(2)–Re(1)–N(1)	174.11(13)	172.8(4)
C(3)–Re(1)–N(1)	97.74(12)	95.8(4)
C(1)–Re(1)–N(1)	92.87(13)	93.6(3)
C(2)–Re(1)–N(2)	99.58(13)	98.4(4)
C(3)–Re(1)–N(2)	172.53(12)	170.5(4)
C(1)–Re(1)–N(2)	91.78(12)	94.2(3)
N(1)–Re(1)–N(2)	74.80(10)	75.3(3)
C(2)–Re(1)–Cl(1)	94.54(11)	91.2(3)
C(3)–Re(1)–Cl(1)	94.85(10)	91.2(3)
C(1)–Re(1)–Cl(1)	174.77(10)	178.3(3)
N(1)–Re(1)–Cl(1)	83.20(8)	84.9(2)
N(2)–Re(1)–Cl(1)	83.87(7)	84.7(2)

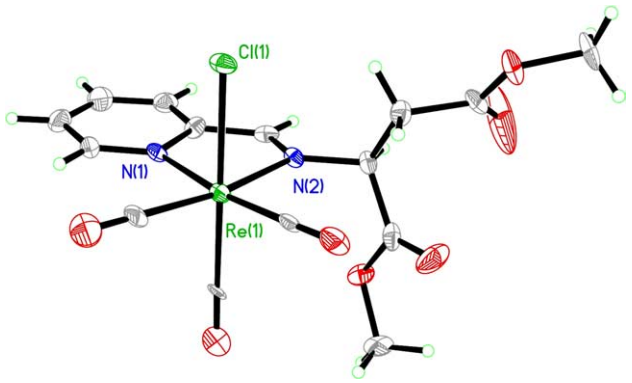

Fig. 4. Molecular structure with 30% thermal ellipsoids for **5**.

N(2)–C(9), N(1)–C(8) and C(9)–C(8) bond lengths of 1.274(4), 1.354(4) and 1.461(5) Å for **2**, and 1.26(1), 1.38(1) and 1.44(2) Å for **5**, respectively, confirm the conjugation of the diimine ligand. The metric data observed for **2** and **5** agree closely with the measurements previously obtained for $Re(CO)_3Cl(pyca\text{-}C_6H_4\text{-}p\text{-}NH_2)$ [27] and are similar to the measurements reported for $Mo(CO)_4$(pyca-β-Ala-OEt) [24].

The ester chains of both **2** and **5** show a tendency to align co-linear to the CO–Re–Cl axis when molecules pack in the crystal. This is similar to the solid state orientations found for $Mo(CO)_4$(pyca-β-Ala-OEt) [24] and the *RS* and *SS* forms of $Mo(CO)_4$(dab-Asp(OMe)-OMe) [25]. This orientation suggests that it may be possible in the future to attach the carboxylate oxygen (or other heteroatom in the side chain) to the metal forming a tridentate ligand. The aspartic acid residue maintains its *S*-stereochemistry [28] in the complex as expected when the synthesis is performed in the absence of NEt_3 [25].

If one considers the three carbonyls as one group, the metal center in these compounds is pseudo-tetrahedral. It is also chiral because the four groups attached to the metal are different.

2.3. Spectroscopic characterization

IR spectra recorded in CH_2Cl_2 displayed three metal carbonyl bands in the region of 2030–1900 cm^{-1}. This is consistent with a pseudo-C_{3v} symmetry for the compounds with an a_1 band and an e band split by the lowering in symmetry [29]. Each spectrum also shows a weaker band around 1735 cm^{-1} due to the amino ester carbonyl.

^{13}C NMR (Table 4) and ^{1}H (Table 5) spectra were acquired for all of the compounds reported. The spectra for all compounds agree in detail with their proposed structures. Spectra of **2** and **4** were easily interpreted. ^{13}C spectra show three metal carbonyl resonances consistent with the pseudo-C_{3v} structure. The two closely spaced downfield peaks are ascribed to the two carbonyls *cis* to the chloride while the upfield resonance is assigned to the carbonyl *trans* to the chloride. The pyridine and imine resonances in the ^{1}H and ^{13}C spectra appear as expected. The imine proton and carbon resonances are diagnostic of the diimine compound bound as a bidentate ligand [25]. The amino ester functionalities occur in expected locations for all compounds indicating that the ligand remains intact.

NMR analysis of compounds **1**, **3**, **5** and **6** shows duplication of some (but not all) peaks in the spectrum-consistent with the presence of diasteromers with unequal populations. Careful integration of appropriate sets of peaks in the ^{1}H NMR spectra shows that the major and minor diastereomers are present in ratios of 56:44 ratio (**1**), 55:45 (**3**), 90:10 (**5**), and 79:21 (**6**), respectively. In contrast, Hodson and co-workers have previously shown that synthesis of $Mo(CO)_2Cl$-(phen)(3-butadienyl-2-CO-Xxx-OR) (phen = 1,10-phenanthroline) yielded pairs of diastereomers in equal proportion [30]. This is likely due to the fact that the chlorocarbonyl precursor, $Mo(CO)_2Cl$(phen)(3-butenyl-2-COCl), is chiral and that the enantiomers are formed in equal proportions. Complete reaction with chiral amino esters leads to equal populations of diastereomeric products.

The unequal populations observed in our work may be attributed to the fact that $Re(CO)_5Cl$ is achiral and

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

	CO_{cis}	CO_{trans}	C^1	C^2	C^3	C^4	C^5	C=N	α-C	β-C	OCO	Other
1 Major	196.8, 195.5	186.4	153.2	128.9	139.1	128.8	155.0	166.4	72.0	18.0	169.8	63.8 CH_2CH_3, 14.0 (CH_3)
Minor[b]	196.4		153.1	128.8		128.7	154.5	168.3		18.7	168.7	62.7 13.9
2	196.7, 196.1	186.4	153.0	128.3	139.2	128.6	154.8	168.7	–[c]	33.1	171. 1	61.1 (CH_2), 60.4 (CH_2), 14.0 CH_3
3 Major	196.3, 195.2	186.5	153.1	128.9	139.1	129.0	154.7	167.9	81.9	30.8	169. 1	53.1 OCH_3, 19.8 CH_3, 18.8 CH_3
Minor[b]				128.8	139.2		154.8	168.1	81.1	32.2	169.5	53.1 19.6 18.7
4	196.8, 196.1	186.6	153.1	128.0	139.2	128.6	154.9	167.1	64.5	–[c]	173. 0	30.6 CH_2, 25.1 CH_2, 51.8 CH_3
5 Major	196.3, 195.2	186.5	153.5	129.4	139.5	129.5	154.5	167.9	72.9	35.5	171.2	53.8 CH_3, 52.6 CH_3,
Minor[b]								167.3	71.5	36.8	168.1	53.6 52.7
6 Major	196.1, 195.2	186.2	153.2	129.1	139.2	128.8	154.2	168.5	74.3	–[c]	170.1	53.3 (OCH_3), 30.1 (CH_2), 28.9 (CH_2), 14.6 (SCH_3)
Minor[b]				129.0	139.1	128.9	154.8	168.7	73.2		168.8	53.4 30.1 29.9 15.2

[a] Recorded in $CDCl_3$. See Fig. 2 for numbering scheme.
[b] Where duplication of peaks is observed, the more intense peak is recorded as the major diastereomer.
[c] CH_2 groups could not be distinguished.

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

	H^1	H^2	H^3	H^4	H–C=N	α-C–H	Other
1 Major	9.04 d (5.5)	7.61 m	8.10 t (7.8)	7.97 t (7.2)	8.96 s	5.15 q (7.0)	4.33 m CH_2, 1.87 d (6.8) $CHCH_3$, 1.38 t (7.2) CH_2CH_3
Minor[b]	9.06 d (5.3)					4.79 q (7.0)	1.79 d (6.8) 1.35 t (7.0)
2	9.02 d (5.5)	7.65 m	8.01 t (7.7)	7.93 t (7.2)	8.96 s	4.41 m	4.13 q (7.0) d (0.8) CH_2CH_3 3.15 m CH_2C=O, 1.24 t (7.2) CH_3
3 Major	9.03 d (5.5)	7.60 m	8.10 t (8.2)	7.98 d (7.8)	9.06 s	4.54 d (9.6)	3.87 s CH_3, 2.66 m CH (CH_3)$_2$, 1.13 d (6.5) 1.01 d (6.5) $CH(CH_3)_2$
Minor[b]					9.17 s	4.58 d (9.8)	3.85 s
4	9.04 d (5.5)	7.60 m	8.09 t (7.8)	7.92 d (7.3)	8.81 s	4.31–4.19 m	3.72 s CH_3, 2.57–2.30 m CH_2–CH_2H_2
5 Major	9.05 d (5.7)	7.62 m	8.10 t (7.7)	8.01 d (7.7)	9.06 s	5.20 m	3.95 s CH_3, 3.70 s CH_3, 3.51 m CH_2
Minor[b]					9.13 s		3.86 s
6 Major	9.06 d (5.5)	7.64 m	8.13 t (7.8)	8.00 d (8.0)	8.95 s	5.06 m	3.88 s OCH_3, 2.75 m CH_2S, 2.57 CH_2 CH_2S, 2.10 SCH_3
Minor[b]					9.04 s		3.87 s 2.71 m 2.14

[a] Recorded $CDCl_3$. See Fig. 2 for adopted numbering scheme.
[b] Where duplication of peaks is observed, the more intense peak is recorded as the major diastereomer.

formation of the stereogenic center leads to the choice of one optical configuration over another based on unknown stereoelectronic factors relating to interactions between the *trans*-chloride/carbonyl ligand pair and the substituents off the α-carbon. It is observed that more unequal populations are observed for **5** and **6**. This suggests that the presence of a polar side group for methionine and aspartic acid exerts more control over the way the bidentate ligand binds to the metal thus affecting the chirality of the resulting metal stereocenter. The small disparity in diastereomer populations measured for **1** and for **3** implies that stereoelectronic differences between the α-hydrogen and the alkyl groups in alanine and valine do not affect the choice of chirality of the metal center.

The electronic absorption spectra of compounds **1**–**6** show an intense absorption band at around 400 nm. The band is tentatively assigned to the $d\pi \rightarrow \pi^*$ (pyca) MLCT transition (Table 6) by comparison with the numerous related compounds of the form, Re(α-diimine)$(CO)_3Cl$, that have been similarly assigned [31–37]. One closely related compound that has been examined previously is Re$(CO)_3$Cl(pyca-*i*-Pr). Its absorbance maxima and extinction coefficient in THF agree closely with the compounds studied here (Table 6) [32]. The MLCT band of the new compounds exhibits a negative solvatochromism in

Table 6
Electronic spectra for compounds **1**–**6** in various solvents

Compound	MeOH[a]	THF	CH_2Cl_2[a]	Δ[b]
1	401 (3.6)	413 (3.7)	424 (3.5)	1353
2	396 (3.8)	405 (3.7)	415 (3.8)	1156
3	408 (3.6)	427 (3.7)	428 (3.8)	1145
4	396 (3.9)	405 (3.6)	416 (3.8)	1214
5	406 (3.4)	424 (3.7)	424 (3.5)	1045
6	401 (3.6)	425 (3.9)	428 (4.0)	1573
$Re(CO)_3Cl$(pyca-*i*-Pr)[c]		411 (3.7)		

[a] λ_{max} in nm (10^3 ε in $M^{-1}cm^{-1}$).
[b] Difference in cm^{-1} between MLCT band in methanol and methylene chloride.
[c] Data taken from [32].

agreement with its charge transfer assignment. This has been observed for similar Re compounds [38] and was also observed in our previous study on group 6 compounds [24,25]. The energy shift for compounds **1**–**6** on changing solvent from CH_2Cl_2 to MeOH is 1.0×10^3–1.6×10^3 cm^{-1}. The shift on moving from toluene to MeOH for the analogous group 6 compounds reported previously ranged from 1.1×10^3 to 1.5×10^3 cm^{-1} [24].

Exploratory photophysical experiments on **2** showed that it was luminescent in air or under nitrogen with a broad emission band centered around 678 ± 3 nm and a lifetime of 28 ± 2 ns for the four solvents tested (Table 7). The wavelength of luminescence is solvent insensitive with the λ_{em} varying by 5 nm. Oxygen quenches the lifetimes by only 5–10%. Many Re(I) compounds are reported to be luminescent even at room temperature [31,39,40]. The literature value for $Re(CO)_3Cl$(bipy) in CH_2Cl_2 is 51 ns. There is a rough correspondence between our absorption/emission data obtained with THF as solvent and the literature values of for $Re(CO)_3Cl$(pyca-*i*-Pr) (Table 7) [32].

2.4. Summary

The previously reported one-pot approach to preparing group 6 diimine bioconjugates has been modified for the rhenium (I) tricarbonyl chloride system. A series of ester-protected amino acid congeners was prepared and characterized in moderate yields. Use of chiral amino esters led to diastereomers because of the stereogenic metal center in the products. Crystal structures of the H-β-Ala-OEt and H-Asp(OMe)-OMe derivatives confirmed the structures of these compounds.

3. Experimental

3.1. Spectroscopic measurements

NMR spectra were recorded on a Varian 400 MHz spectrometer. IR spectra were recorded on a Nicolet Series II Magna-IR 750 spectrometer and electronic spectra were obtained with a Hitachi U-2000 spectrometer. Elemental Analysis were performed by Atlantic Microlab of Norcross, GA 30091. Fluorescence data were collected on a Jobin Yvon Fluorolog-3 (FL3-22) spectrometer equipped with a 450 W Xenon lamp as the source. Data were processed with the DataMax for Windows software program.

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. $Re(CO)_5Cl$ was prepared by a modification to the literature procedure in which $CHCl_3$ was substituted for CCl_4 [29].

Table 7
Luminescence data obtained for **2** at 298 K

Compound	Solvent	λ_{max} (nm)	λ_{em} (nm)	Δ (10^3 cm^{-1})[a]	FI[b]	τ_0 (298), ns[c]
2	MeOH	395	676	10.5	0.79	26
2	Acetone	400	679	10.3	0.76	28
2	THF	412	681	9.6	0.74	28
2	CH_2Cl_2	414	678	9.4	1.00	30
$Re(CO)_3Cl$(pyca-*i*-Pr)[a]	THF	394	605	8.9		

[a] Performed at 80 K. Data from [32].
[b] Relative emission intensities.
[c] Lifetime (ns).

3.3. Synthesis of 1–6

Maximum yields were obtained by mixing the chemicals needed to form the ligand prior to adding the metal reagent. In a typical procedure, the amino acid ester, H–Xxx–OR · HCl (0.829 mmol) and pyridine-2-carboxaldehyde (0.0888 g, 0.829 mmol), were added to 20 ml of methanol. The solution was stirred at room temperature under nitrogen for 20 minutes. Upon addition of $Re(CO)_5Cl$ (0.150 g, 0.415 mmol), the solution was heated to reflux. After 4–5 h, the solution was bright red. Solvent was removed with a rotary evaporator. Immediate crystallization occurred. The compound was purified via flash chromatography. CH_2Cl_2 (20 mL) and silica gel (6 mL) were added to the residue. The solvent was removed. The reaction mixture bound to the silica gel was placed on top of a (50 mL) column of dry silica gel. Separation of the orange product band from impurities was achieved using 2:1 ethyl acetate:hexane. Solvent was removed by rotary evaporator. The product was recrystallized by dissolving the product in CH_2Cl_2, and layering hexane over the surface of the solution. The flask was placed in the freezer overnight. Filtration and drying left a red or orange crystalline solid.

1: 53% yield. IR (CH_2Cl_2): 2027 (vs), 1926 (s), 1905 (s), 1742 (m, ester) cm^{-1}. Anal. Calc. for $C_{14}H_{14}ClN_2O_5Re$; C, 32.85; H, 2.76; N, 5.47. Found: C, 32.80; H, 2.73; N, 5.44%. A 56:44 ratio of diastereomers was determined by integration of the methyl proton resonances on the β-carbon in the ^1H NMR spectrum.

2: 86% yield. IR (CH_2Cl_2): 2025 (vs), 1925 (s), 1902 (s), 1730 (m, ester) cm^{-1}. Anal. Calc. for $C_{14}H_{14}ClN_2O_5Re$; C, 32.85; H, 2.76; N, 5.47. Found: C, 33.09; H, 2.73; N, 5.50%.

3: 86% yield. IR (CH_2Cl_2): 2027 (vs), 1928 (s), 1903 (s), 1740 (m, ester) cm^{-1}. Anal. Calc. for $C_{15}H_{16}ClN_2O_5Re$; C, 34.25; H, 3.07; N, 5.33. Found: C, 34.34; H, 3.10; N, 5.31%. A 55:45 ratio of diastereomers was determined by integration of the iso-propyl methyl protons in the ^1H NMR spectrum.

4: 69% yield. IR (CH_2Cl_2): 2025 (vs), 1925 (s), 1901 (s), 1735 (m, ester) cm^{-1}. Anal. Calc. for $C_{14}H_{14}ClN_2O_5Re$; C, 32.85; H, 2.76; N, 5.47. Found: C, 33.02; H, 2.75; N, 5.46%.

5: 53% yield. IR (CH_2Cl_2): 2028 (vs), 1928 (s), 1906 (s), 1736 (m, ester) cm^{-1}. Anal. Calc. for $C_{15}H_{14}ClN_2O_7Re$; C, 32.40; H, 2.54; N, 5.04. Found: C, 32.13; H, 2.64; N, 4.92%. A 90:10 ratio of diastereomers was determined by integration of the resonances assigned to the methyl ester attached to the α-carbon.

6: 47% yield. IR (CH_2Cl_2): 2027 (vs), 1928 (s), 1903 (s), 1740 (m, ester) cm^{-1}. Anal. Calc. for $C_{15}H_{16}ClN_2O_5SRe$; C, 32.28; H, 2.89; N, 5.02. Found: C, 32.56; H, 2.93; N, 5.13%. A 79:21 ratio of diastereomers was determined by integration of the methyl thioether resonances in the ^1H NMR spectrum.

3.4. X-ray structure determination of 2 and 5

Crystals for crystallographic analysis were mounted on a cryoloop using Paraton N-Exxon oil and placed under a stream of cold nitrogen gas. Analyses of the data sets showed negligible decay during data collection. The data were corrected for absorption using the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.10) and were solved until the final anisotropic full-matrix, least squares refinement of F^2 converged [41]. Additional experimental details are provided in Table 2.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, nos. 246099 and 246100 for **2** and **5**, respectively. 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; email: deposit@ccdc.cam.a-c.uk or http://www.ccdc.cam.ac.uk).

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