Dinuclear Pentamethylcyclopentadienyl Rhodium and Iridium Complexes from C=C-Bridged Amino Acid Dimers[‡]

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Dedicated to Professor Marianne Baudler on the occasion of her 80th birthday

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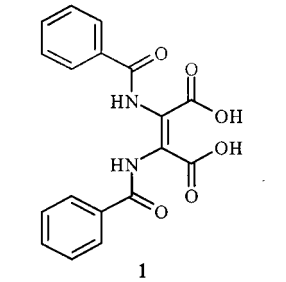
Hippuric acid dimers bridged by a C=C double bond react with the chloro-bridged complexes $(Cp^*)(Cl)M(\mu\text{-}Cl)_2M(Cp^*)(Cl)$ with decarboxylation or loss of a benzoyl group to give the unexpected ligand-bridged dinuclear complexes **2** and **4**, which were characterized by X-ray diffraction. In the iridium complex **2** an oxazolone derivative forms a C,O-N,N′-coordinated bridge, whereas in the rhodium complex **4** a chlorine atom and an amide group bridge the two metal atoms.

Recently, the synthesis and characterization of α-amino acid and peptide dimers bridged by C=C double bonds was reported.[1] These dimers are formed as *Z* and *E* isomers by condensation of α-chloroglycine derivatives with triphenylphosphane and base and are of interest for peptides with a cross-linked backbone. We investigated the coordination behavior of these novel compounds in order to get information on the configuration at the C=C bond of the amino acid dimers. By reaction of chloro-bridged, half-sandwich complexes of rhodium, iridium and ruthenium of the type $(L)ClM(\mu\text{-}Cl)_2M(L)Cl$ with α-amino acids and peptides a series of organometallic N,O- and N,N′-chelate complexes was obtained.[2]

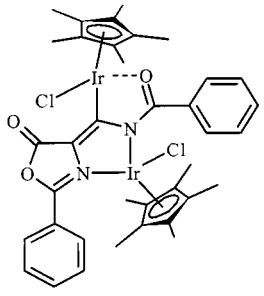
Using this established strategy, the chloro-bridged pentamethylcyclopentadienyl iridium complex $Cp^*(Cl)Ir(\mu\text{-}Cl)_2Ir(Cl)(Cp^*)$ was reacted with the dimeric hippuric acid derivative **1** in the presence of NaOMe or LiOH. Compound **1** was prepared by hydrolysis of the corresponding *Z*-configured dimethyl ester.[1]

The reaction resulted in the formation of the unexpected product **2**, whose structure was solved by X-ray diffraction (Figure 1). Formation of complex **2** occurs by decarboxylation of one carboxylic group of **1** and formation of an oxazolone ring. Decarboxylation is typical for α,β-unsaturated carboxylic acids.[3] Oxazolones are usually formed by dehydration of *N*-acyl-α-amino acids with carbodiimides or carboxylic acid anhydrides.[4] Cyclization to an oxazolone to give **2** is obviously favorable in the coordination sphere of a metal. The X-ray structure determination also reveals metalation at the former C=C bridge of **1**. It is worthwhile to note that the reactions of the dimer $[Cp^*IrCl_2]_2$ with substituted oxazolones afforded either orthometalation [5] or metalation of the oxazolone ring.[6]



1

1. NaOMe
2. $[Cp^*IrCl_2]_2$



2

Complex **2** contains two different stereogenic centers at the iridium atoms, and the two expected diastereoisomers (as pairs of enantiomers) are observed in the ^1H NMR spectrum. Each diastereoisomer should exhibit two ^1H NMR signals for the nonequivalent Cp* units. In fact four ^1H NMR singlets (δ = 0.97, 1.07, 1.75 and 1.85) are found

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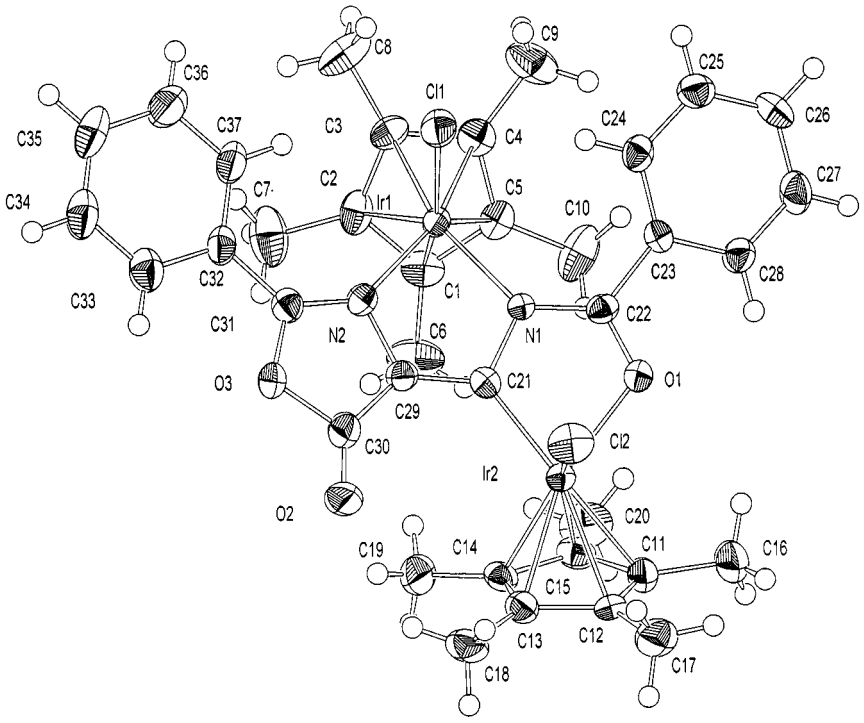


Figure 1. Molecular structure of **2** in the crystal; selected bond lengths (Å), angles (°) and torsion angles (°): Ir1−N2 2.103(5), Ir2−O1 2.083(4), Ir1−Cl1 2.411(2), Ir2−Cl2 2.404(2), N2−C31 1.312(8), C21−C29 1.382(8), C22−O1 1.272(7), Ir1−N1 2.156(5); Cl1−Ir1−N1 92.82(13), N2−C29−C21 120.5(5), N1−C22−O1 120.0(5), Ir2−C21−C29 131.9(5), N2−C29−C21−N1 2.09, Cl2−Ir2−C21 91.0(2), N1−Ir1−N2 76.1(2), Ir2−C21−C29−C30 12.68(6), C21−N1−C22−O1 5.50(5)

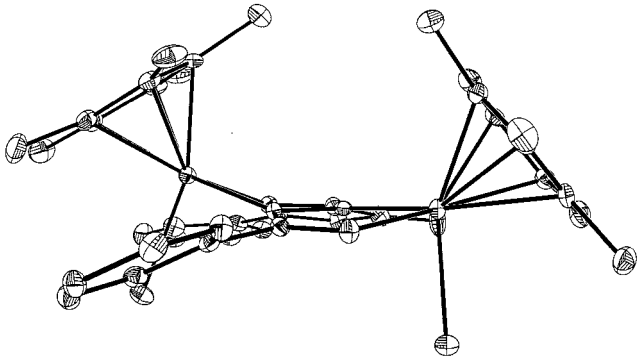


Figure 2. Side view of the molecular structure of **2** in the crystal

in the spectrum of the solution of product **2**. The two diastereoisomers could be separated: from a methanol solution of **2** only one diastereoisomer crystallized, and the crystal of **2** contained only one diastereoisomer as a racemate R_{Ir1}-S_{Ir2} and $S_{Ir1}R_{Ir2}$. In Figure 1 the $S_{Ir1}R_{Ir2}$ isomer is shown. As expected, the solution of the crystal exhibited only two Cp* ^{1}H NMR signals at δ = 1.07 and 1.85. In the ^{13}C NMR spectra the high downfield shift of the NMR signal for the metalated carbon atom at δ = 206 is remarkable, which corresponds to a quite short Ir2−C21 bond length of 1.995(6) Å (Figure 1) in the crystal. For the above-mentioned oxazolones a signal in the area of δ = 70 and 174 was observed.[5,6] On the other hand, the central C=C bond (C21−C29) is, with 1.382(8) Å, longer than the uncomplexed amino acid dimer (1.32−1.33 Å[1,8]). Figure 2 shows a side view of **2** demonstrating the almost planar arrangement of the novel bridging ligand.

A second unexpected product is formed from the reaction of the amino acid dimer **3** with $[Cp^*RhCl_2]_2$ in the presence of NaOMe. It is a chloro- and amido-bridged[7] dinuclear complex **4**, which is formed by cleavage of one benzoyl group from **3** and which was also characterized by X-ray structure determination (Figure 3, Table 1).

The fourth coordination sites of the rhodium atoms are occupied by a carboxylate oxygen donor and a chloro ligand. The formation of **4** involves a $Z \rightarrow E$ isomerization[1] of the amino acid dimer **3**. In the crystal of **4** both enantiomers $R_{Rh1}R_{Rh2}$ and $S_{Rh1}S_{Rh2}$ are present giving rise to two Cp* ^{1}H NMR signals in solution. In Figure 2 the structure of the $R_{Rh1}R_{Rh2}$ isomer with the chiral N1 atom in the *S* configuration is shown. Two hydrogen bonds NH···O−C(O) which fix the amino acid dimer in the *E* configuration can be detected both in solution and in the crystal. The two NH signals appear at rather low field (δ = 10.8 for the bridging amide and δ = 8.21 for the uncoordinated amide group) in the ^{1}H NMR spectra, and relatively short distances N1(H1)···O4 (2.244 Å) and N2(H2)···O2 (2.114 Å) are found in the solid. The crystal data show only a slight elongation of the central C=C bond [C22−C23 1.360(9) Å] in **4**. In both dinuclear complexes **2** and **4** the metal atoms have a distorted tetrahedral environment.

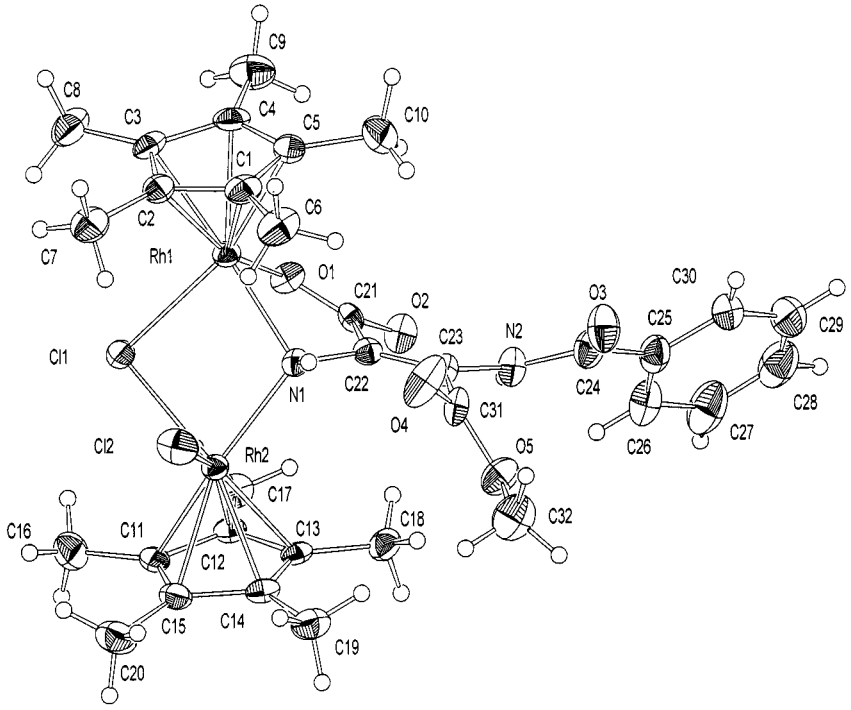
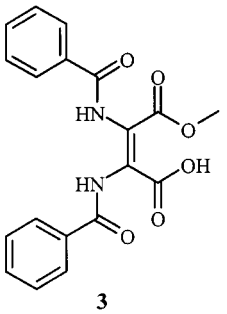


Figure 3. Molecular structure of **4** in the crystal; selected bond lengths (Å), angles (°) and torsion angles (°): Rh1−Cl1 2.441(2), Rh1−N1 2.109(5), Rh1−O1 2.119(5), Rh2−Cl1 2.485(2), Rh2−N1 2.145(5), Rh2−Cl2 2.402(3), N1−C22 1.418(8), C22−C23 1.360(9), C21−C22 1.518(9), C21−O1 1.221(8), C21−O2 1.248(7), H1(N1)−O4 2.244, H2(N2)−O2 2.114, Cl1−Rh1−O1 87.9(2), Cl1−Rh1−N1 84.2(2), N1−Rh1−O1 77.7(2), Cl1−Rh2−N1 82.7(2), N1−C22−C23 124.2(6), N1−C22−C21 112.5(5), O1−C21−O2 125.7(6), O1−C21−C22 115.8(6), N1−C22−C21−O1 25.0(6), N1−C22−C23−C31 2.11(5), N1−Rh2−Cl1−Rh1 2.9(2), Rh1−N1−C22−C21 41.8(6)

Table 1. Crystallographic data of **2** and **4**[10]

Empirical formula	$C_{32}H_{40}Cl_2N_2O_5Rh_2$	$C_{37}H_{40}Cl_2Ir_2N_2O_3$
Molecular weight	809.38	1016.01
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	*P*21/*c*	$P\bar{1}$
Unit cell dimensions	*a* = 12.303(6) Å	*a* = 10.482(2) Å
	α = 90°	α = 91.006(13)°
	b = 14.086(10) Å	*b* = 11.210(2) Å
	β = 91.41(3)°	β = 94.215(13)°
	c = 19.482(7) Å	*c* = 15.785(2) Å
	γ = 90°	γ = 115.10(2)°
Volume	3375(3) Å^3	1672.7(5) Å^3
Z	4	2
Density (calculated)	1.593 Mg/m^3	2.017 Mg/m^3
Absorption coefficient	1.177 mm^{-1}	8.148 mm^{-1}
F(000)	1640	976
Crystal size	0.53 × 0.27 × 0.07 mm	0.27 × 0.13 × 0.07 mm
Theta range for data collection	2.54 to 24.98°	2.15 to 23.97°
Index ranges	$-14 \le h \le 0$	$-11 \le h \le 11$
	$-16 \le k \le 0$	$-12 \le k \le 12$
	$-23 \le l \le 23$	$-18 \le l \le 0$
Reflections collected	6218	5440
Independent reflections	5921 [*R*(int) = 0.0234]	5224 [*R*(int] = 0.0174
Absorption correction	Semi-empirical from ψ-scans	Semi-empirical from ψ-scans
Max. and min. transmission	0.9992 and 0.8716	0.9999 and 0.7075
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5921/0/399	5224/0/425
Goodness-of-fit on F^2	1.181	1.106
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0520, *wR*2 = 0.0988	*R*1 = 0.0253, *wR*2 = 0.0468
R indices (all data)	*R*1 = 0.0880, *wR*2 = 0.1125	*R*1 = 0.0406, *wR*2 = 0.0522
Largest diff. peak and hole	0.942 and −0.457 e·Å^{-3}	0.578 and −0.615 e·Å^{-3}



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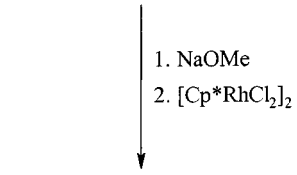

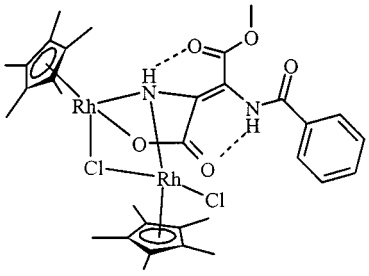

4

Conclusion

Different products were obtained from the reactions of the C=C-bridged amino acid dimers **1** and **3** with chloro-bridged complexes. Protection of one carboxylic group by esterification in **3** prevents decarboxylation and formation of an oxazolone ring as was observed with **1**. One can speculate why the two reactions proceed so differently. An explanation could arise if one considers the first step of these reactions. With **1** formation of an N,N(amide) and an O,O(carboxylate) chelate diiridium complex seems possible, which, after decarboxylation of one carboxylic group followed by metalation at the C=C bond and condensation of the benzoyl and carboxylic groups, gives the product **2**. Coordination of the two former amide nitrogen atoms of the *Z* amino acid dimer is found in the product **2**. In contrast, **3** can coordinate in the first step through the amide and carboxylate group of one half of the *Z*-amino acid dimer to form a chelate, as is present in product **4**. The noncoordinated second half of the amino acid dimer with the carboxylic ester can then undergo the $Z \rightarrow E$ isomerization which is necessary to form product **4**. Base-induced $Z \rightarrow E$ isomerization of C=C-bridged amino acid dimers has already been observed.[8] The fate of the lost benzoyl group remains unclear.

Experimental Section

NMR measurements were recorded on Jeol GSX 270 and Jeol EX 400 spectrometers. IR analyses were obtained on a Nicolet 520 FT-IR spectrometer. FAB MS was performed on a Finnigan MAT 90 instrument. The X-ray structure determination was carried out with a NONIUS CAD4 diffractometer. The dimeric hippuric acid derivatives **1** and **3** were prepared by deprotection of (*Z*)-2,3-bis(*N*,*N*′-benzoylamino)maleic acid dimethyl ester, which was synthesized according to a literature procedure.[9]

To a suspension of the dimethyl ester (382 mg, 1 mmol) in THF (9 mL) and water (3 mL) was added LiOH (72 mg, 3 mmol) at 0 °C and the mixture was stirred overnight. The resulting solution was acidified to pH 2 with a 1.1 M solution of $KHSO_4$ and extracted three times with ethyl acetate (20 mL). The combined organic fractions were washed with 20 mL of water and 20 mL of brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure yielded the free acid **1** which was used without further purification. If the deprotection reaction was carried out with a molar ratio dimethyl ester/LiOH of 1:1 the main product was (*Z*)-2,3-bis(*N*,*N*′-benzoylamino)maleic acid mono methyl ester **3**, which was isolated by column chromatography.

2: A solution of (*Z*)-2,3-bis(*N*,*N*′-benzoylamino)maleic acid (**1**; 54 mg, 0.15 mmol) in 5 mL of methanol was stirred with a 1.65 M solution of NaOMe in methanol (185 μL, 0.30 mmol). $[Cp^*IrCl_2]_2$ [10] (121 mg, 0.15 mmol) was added to the resulting yellow solution and the mixture stirred for an additional 15 min. The resulting orange solution was set aside overnight leading to the precipitation of orange crystals suitable for X-ray diffraction. Yield 67 mg (44%). − IR (KBr): $\tilde{\nu}$ = 3063 w, 2918 w, 1776 vs (C=O), 1742 m, 1606 w (C=N), 1590 m, 1469 vs, 1392 s, 1374 s, 1162 m, 1073 m 834 m, 702 cm^{-1} m. − ^1H NMR (270 MHz, CD_2Cl_2): δ = 1.07 [s, 15 H, $C_5(CH_3)_5$], 1.85 [s, 15 H, $C_5(CH_3)_5$], 7.43−7.57 (m, 6 H, *m*- and *p*-C_6H_5), 8.44−8.52 (m, 4 H, *o*-C_6H_5). − ^{13}C NMR (67.9 MHz, CD_2Cl_2): δ = 8.6 [$C_5(CH_3)_5$], 8.9 [$C_5(CH_3)_5$], 86.8 [$C_5(CH_3)_5$], 90.1 [$C_5(CH_3)_5$], 125.7 (*C*=C), 126.6, 127.9, 128.7, 130.3, 131.5, 131.7, 132.3, 134.1 (Ph), 154.7 (C=N), 163.4 (CO_2), 187.0 (CON), 205.9 (C-Ir). − MS(FAB): *m*/*z* = 1016 (17) $[M]^+$. − $C_{37}H_{40}Cl_2Ir_2N_2O_3$ (1016.01): calcd. C 43.74, H 3.97, N 2.76; found C 43.90, H 3.97, N 2.75.

4: A solution of (*Z*)-2,3-bis(*N*,*N*′-benzoylamino)maleic acid monomethyl ester (**3**; 30 mg, 0.08 mmol) in 7 mL of methanol was stirred with a 1.65 M solution of NaOMe in methanol (99 μL, 0.16 mmol). $[Cp^*RhCl_2]_2$ [10] (50 mg, 0.08 mmol) was added to the resulting yellow solution and the mixture stirred overnight. The solvent was removed in vacuo and the residue redissolved in 3 mL of dichloromethane. The red solution was filtered through Celite and concentrated under reduced pressure. Recrystallisation from dichloromethane/*n*-hexane yielded red crystals suitable for X-ray analysis. Yield 22 mg (34%). − IR (KBr): $\tilde{\nu}$ = 3296 w, 2958 w, 2917 m, 2851 m, 1725 w, 1692 w, 1664 s, 1601 vs, 1588 vs, 1540 m, 1478 vs, 1455 vs, 1443 m, 1375 s, 1310 s, 1264 m, 1161 m, 1080 m, 1025 s, 933 w, 801 m, 717 s, 615 cm^{-1} m. − ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.41 [s, 15 H, $C_5(CH_3)_5$], 1.55 [s, 15 H, $C_5(CH_3)_5$], 3.86 (s, 3 H, OCH_3), 7.45−7.57 (m, 3 H, *m*- and *p*-C_6H_5), 7.91−7.94 (m, 2 H, *o*-C_6H_5), 8.21 (d, ^3J = 9.2 Hz, 1 H, NH), 10.81 (s, 1 H, NH−Rh). − ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 8.4 [$C_5(CH_3)_5$], 8.5 [$C_5(CH_3)_5$], 52.1 (OCH_3), 92.9 [d, J_{RhC} = 9.3 Hz, $C_5(CH_3)_5$], 93.9 [d, J_{RhC} = 8.4 Hz, $C_5(CH_3)_5$], 117.5 (*C*=C), 127.5, 128.6, 131.8, 133.6 (Ph), 164.9 (CON), 166.1 (CO_2CH_3), 173.7 (CO_2). − MS (FAB): *m*/*z* = 809 (2) $[M]^+$, 774 (23) $[M - Cl]^+$.

Acknowledgments

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[11] Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-152476 (**2**) and -152477 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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