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## Synthesis and Reactivity of $\eta^4$ -Diene-Fe(CO)<sub>3</sub> Complexes from *exo*-2-Oxazolidinone Dienes. A Facile Generation of Stable Conjugated Enol-Enamido Species

Fernando Ortega-Jiménez,<sup>†,§</sup> Adriana Benavides,<sup>†</sup> Francisco Delgado,<sup>\*,†</sup>  
Hugo A. Jiménez-Vázquez,<sup>†</sup> and Joaquín Tamariz<sup>\*,†</sup>

<sup>†</sup>Departamento de Química Orgánica, Escuela Nacional de Ciencias Biológicas-IPN, Prol. Carpio y Plan de Ayala, 11340 México, D. F., Mexico and <sup>§</sup>Departamento de Ciencias Químicas, Facultad de Estudios Superiores Cuautitlán-UNAM, Campo 1, Cuautitlán Izcalli, Estado de México, 54740, Mexico

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A synthesis of new  $\eta^4$ -diene-Fe(CO)<sub>3</sub> complexes derived from the novel *exo*-2-oxazolidinone dienes is described. These complexes were prepared by thermal complexation of the substituted dienes with diiron nonacarbonyl to afford the corresponding complexes as crystal solids. The X-ray single-crystal structure analysis revealed characteristic structural properties for diene-iron complexes, showing that in the conformation of the distorted trigonal-pyramidal geometry two of the carbonyl groups point out from the metal toward the vertex C4 and C5 atoms of the heterocycle. Unsuccessful functionalization of the diene moiety by acylation or alkylation of the allylic position indicated the strong stability of these dienes. This stability facilitated the generation of stable and unprecedented conjugated enamine-enol ester- and enamido-enol-Fe(CO)<sub>3</sub> complexes, by either kinetic or thermodynamic control of the reaction conditions.

### Introduction

The Fe(CO)<sub>3</sub> group has been traditionally used as a protecting group for conjugated dienes, as ( $\eta^4$ -1,3-diene)-Fe(CO)<sub>3</sub> complexes.<sup>1</sup> These complexes are stable enough to allow the interconversion of functional groups (FGI) into the same molecule with a variety of reactions such as oxida-

tions,<sup>2</sup> reductions,<sup>3</sup> alkylations,<sup>4</sup> and cycloadditions,<sup>4c,5</sup> among others (Scheme 1).<sup>6</sup> The Fe(CO)<sub>3</sub> group can also promote the stabilization of unstable dienes or dienic tautomers.<sup>7</sup> Moreover, the complex can be directly involved in the functionalization of the diene through diverse reactions; for instance, acylation,<sup>8</sup> cyclocarbonylation,<sup>7a,9</sup> formylation,<sup>10</sup> alkylation,<sup>11</sup> and isomerization (Scheme 1).<sup>12</sup> The fact that the deprotection of the  $\eta^4$ -diene-Fe(CO)<sub>3</sub> complexes is an easy, practical, and efficient reaction converts these complexes into a very attractive protecting group and synthons in organic synthesis.<sup>13</sup>

\*Corresponding authors. Fax: (+52)55-5729-6300/46211. E-mail: jtamariz@woodward.encb.ipn.mx; fdelgado@woodward.encb.ipn.mx.

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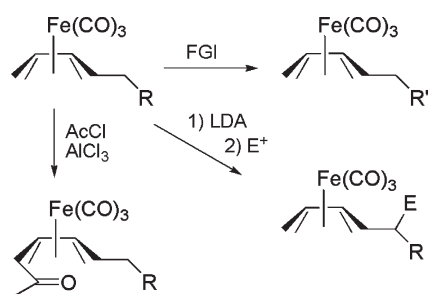
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**Scheme 1. Diene Protecting and Activating  $\text{Fe}(\text{CO})_3$  Group in Transformation of Vicinal Functional Groups, as Well as Acylation and Deprotonation/Electrophilation Reactions**

We have developed a tandem methodology to prepare the novel *N*-substituted *exo*-2-oxazolidinone dienes **3–5**,<sup>14</sup> which involves a base-assisted condensation of  $\alpha$ -diketones **2** and isocyanates **1** in the presence of a dehydrating agent (Scheme 2). The use of the unsymmetrical  $\alpha$ -diketones **2b** and **2c** under similar reaction conditions furnished dienes **4** and **5** as a single regio- and stereoisomer.<sup>14b,c</sup> This methodology has been successfully applied to the synthesis of 1,4-dimethyl-substituted dienes<sup>15</sup> and also of those analogues containing the dienic moiety in a six-membered ring.<sup>16</sup> Dienes **3** and **4** have proved to be useful synthons in the preparation of carbazoles,<sup>17</sup> leading to the total synthesis of a series of naturally occurring carbazoles.<sup>18</sup> Moreover, they have been converted into new polycyclic oxazol-2-one derivatives by a tandem [4+2] cycloaddition/cyclopentannulation/1,5-sigmatropic rearrangement process with Fischer (aryalkynyl)(alkoxy)carbenes<sup>19</sup> and have turned out to be efficient substrates for the synthesis of  $\eta^4$ : $\pi^2$ -diene-iridium(I) complexes, whose reactivity with alkynylphosphines and aldehydes was also studied.<sup>20</sup>

With the aim of evaluating the stability and versatility of *exo*-2-oxazolidinone dienes **3–5**, herein we describe the synthesis, structural characterization, and spectral properties of the new ( $\eta^4$ -1,3-diene)- $\text{Fe}(\text{CO})_3$  complexes **6–8**, as well as the study of their reactivity toward acylation and alkyllithium addition reactions.

## Results and Discussion

### Preparation of ( $\eta^4$ -*exo*-4-Methylene-5-alkylidene-2-oxazolidinone)- $\text{Fe}(\text{CO})_3$ Complexes **6–8**. Evidence of the thermal

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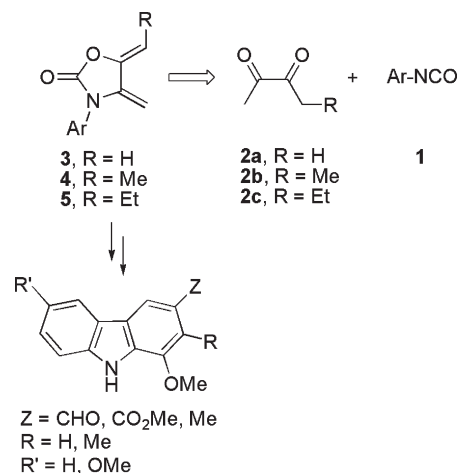
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**Scheme 2. Synthesis of Dienes **3–5** from **1** and **2** and Their Conversion to Natural Carbazoles**

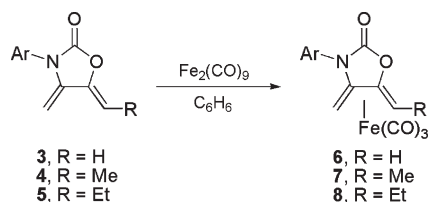
stability of dienes **3–5** was gathered from the Diels–Alder addition to activated alkenes with electron-withdrawing groups, such as methyl vinyl ketone<sup>14</sup> and alkyl acrylates,<sup>18a</sup> at high temperatures to afford the corresponding cycloadducts in modest to good yields. Hence, by treatment of the dienes with diiron nonacarbonyl in benzene at reflux, the series of  $\text{Fe}(\text{CO})_3$  complexes **6a–e**, **7a–e**, and **8a–e** were obtained in moderate to good yields (Table 1). It is noteworthy that the novelty of these compounds resides, among other features, in the fact that, to best of our knowledge, there are few reports of  $\text{Fe}(\text{CO})_3$  complexes of exocyclic dienes substituted by two heteroatoms.<sup>21</sup>

Actually, the general procedure was established by optimizing the preparation of complex **6a** (Table 1, entries 1–3), in which the best molar ratio for the mixture diene/ $\text{Fe}_2(\text{CO})_9$  was 1:3, and the reaction temperature was set to that of the refluxing solvent. Under these conditions, the reaction time was shortened to 3 h, providing the best yield. However, the efficiency of the procedure for the other analogues was not the same, even changing some parameters of the reaction. Although the yields were moderate for most of the cases, the best ones were observed only for diene complexes **6a** and **7a**. No correlation was found between yields and the kind or position of the substituent in the benzene ring (Table 1). For instance, the presence of a methyl group at the *ortho* position, which can be expected to be more hindered, did not significantly deplete the yield. In general, the reaction was clean and almost no side products were detected, recovering the unreacted starting dienes. A longer reaction time or further addition of  $\text{Fe}_2(\text{CO})_9$  did not improve the conversion rate.

It should be noted that *ortho*-substituted *N*-aryl complexes **6b**, **7b**, and **8b** were obtained as an inseparable mixture of atropoisomers in about a 64:36 ratio. Structural analysis by spectroscopy did not provide evidence about the relative configuration of the major rotamer. However, it is expected that the latter corresponds to the less hindered *anti* isomer (the methyl group with respect to the  $\text{Fe}(\text{CO})_3$  group).

**Electronic Absorption, Infrared, and NMR Spectra of Complexes **6–8**.** Ultraviolet (UV) spectra of dienes **3a**, **4a**, and **5a** and of complexes **6a**, **7a**, and **8a** were measured in acetonitrile as the solvent. The spectra of the dienes are

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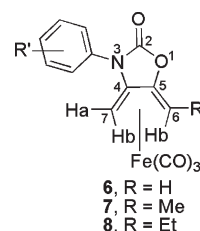
**Table 1.** Preparation of  $\eta^4$ -Diene  $\text{Fe}(\text{CO})_3$  Complexes **6a–e**, **7a–e**, and **8a–e**<sup>a</sup>

entry	diene	Ar	T (°C)	t (h)	complex	Mp (°C)	yield (%) <sup>b</sup>
1	<b>3a</b>	C <sub>6</sub> H <sub>5</sub>	40	12	<b>6a</b>	119–120	60
2	<b>3a</b>	C <sub>6</sub> H <sub>5</sub>	60	8	<b>6a</b>	119–120	65
3	<b>3a</b>	C <sub>6</sub> H <sub>5</sub>	80	3	<b>6a</b>	119–120	75
4	<b>3b</b>	C <sub>6</sub> H <sub>4</sub> -2-Me	80	3	<b>6b</b>	158–160	42
5	<b>3c</b>	C <sub>6</sub> H <sub>4</sub> -4-Me	80	3	<b>6c</b>	123–124	53
6	<b>3d</b>	C <sub>6</sub> H <sub>4</sub> -3-Cl	80	3	<b>6d</b>	110–111	38
7	<b>3e</b>	C <sub>6</sub> H <sub>4</sub> -4-Cl	80	3	<b>6e</b>	107–108	40
8	<b>4a</b>	C <sub>6</sub> H <sub>5</sub>	80	3	<b>7a</b>	163–164	86
9	<b>4b</b>	C <sub>6</sub> H <sub>4</sub> -2-Me	80	3	<b>7b</b>	158–160	43
10	<b>4c</b>	C <sub>6</sub> H <sub>4</sub> -4-Me	80	3	<b>7c</b>	102–103	63
11	<b>4d</b>	C <sub>6</sub> H <sub>4</sub> -3-Cl	80	3	<b>7d</b>	161–163	48
12	<b>4e</b>	C <sub>6</sub> H <sub>4</sub> -4-Cl	80	3	<b>7e</b>	105–106	36
13	<b>5a</b>	C <sub>6</sub> H <sub>5</sub>	80	3	<b>8a</b>	126–127	58
14	<b>5b</b>	C <sub>6</sub> H <sub>4</sub> -2-Me	80	3	<b>8b</b>	113–115	48
15	<b>5c</b>	C <sub>6</sub> H <sub>4</sub> -4-Me	80	3	<b>8c</b>	113–114	52
16	<b>5d</b>	C <sub>6</sub> H <sub>4</sub> -3-Cl	80	3	<b>8d</b>	121–122	59
17	<b>5e</b>	C <sub>6</sub> H <sub>4</sub> -4-Cl	80	3	<b>8e</b>	127–128	48

<sup>a</sup> Conditions:  $\text{Fe}_2(\text{CO})_9$  (3.0 mol equiv), benzene, reflux,  $\text{N}_2$  atm.<sup>b</sup> Calculated after recrystallization.

similar between them, showing three separate high-intensity bands in the range 204–209, 227–233, and 257–264 nm, where the first and the latter are attributed to the aromatic  $\pi \rightarrow \pi^*$  transitions, and the central one is due to the diene  $\pi \rightarrow \pi^*$  transition (the calculated wavelength is about 229 nm).<sup>22</sup> In the case of the spectra of complexes, the carbonyl  $n \rightarrow \pi^*$  transitions of the  $\text{Fe}(\text{CO})_3$  group appear as a low-intensity long-wavelength band at about 309–314 nm as a tail of the high-intensity band.<sup>23</sup> The latter is a broad band showing a maximum and two additional absorptions as well-defined shoulders, which are due to the overlapping of aromatic and diene  $\pi \rightarrow \pi^*$  transitions.<sup>24</sup>

The infrared (IR) spectra of the  $\text{Fe}(\text{CO})_3$  complexes are also similar between them. Strong bands appear in the spectrum between 2100 and 1900  $\text{cm}^{-1}$ , which correspond to the characteristic stretching frequencies of the carbonyl groups of the  $\text{Fe}(\text{CO})_3$  moiety.<sup>25</sup> In addition, in the region of 1790–1750  $\text{cm}^{-1}$ , the spectra show a strong absorption due to the C=O stretching mode of the carbamate heterocycle.

**Table 2.**  $^1\text{H}$  NMR Selected Data of the Dienes **3a**, **4a**, and **5a** and  $\eta^4$ -Diene- $\text{Fe}(\text{CO})_3$  Complexes **6a–e**, **7a–e**, and **8a–e**<sup>a</sup>

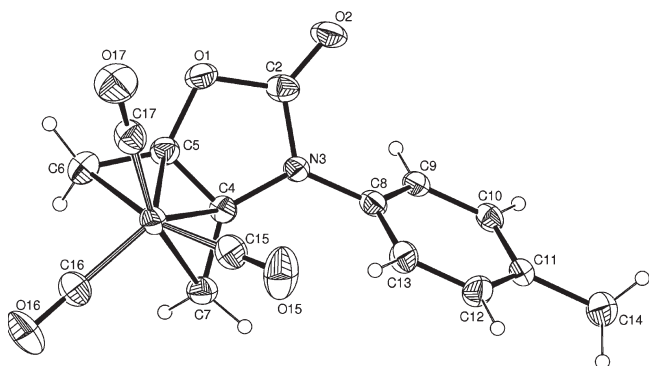
diene	$\delta$ (ppm)			
	H-7a <sup>b</sup>	H-7b <sup>b</sup>	H-6b <sup>c</sup>	R <sup>d</sup>
<b>3a</b> <sup>e</sup>	4.35	4.76	4.98	4.93
<b>4a</b> <sup>e</sup>	4.18	4.58	5.42	1.86
<b>5a</b> <sup>f</sup>	4.19	4.59	5.38	2.33
<b>6a</b>	2.17	0.33	0.51	2.59
<b>6b</b>	1.90	0.30	0.50	2.59
<b>6c</b>	2.13	0.30	0.50	2.58
<b>6d</b>	2.17	0.34	0.52	2.60
<b>6e</b>	2.13	0.32	0.51	2.60
<b>7a</b>	2.05	0.20	1.27	1.83
<b>7b</b>	1.78	0.19	1.27	1.84
<b>7c</b>	2.02	0.19	1.27	1.83
<b>7d</b>	2.07	0.22	1.29	1.83
<b>7e</b>	2.02	0.21	1.29	1.83
<b>8a</b>	2.06	0.20	1.17	2.24–2.34
<b>8b</b>	1.80	0.19	1.14–1.23	2.01–2.19
<b>8c</b>	2.03	0.18	1.15	2.02–2.13
<b>8d</b>	2.02–2.14 <sup>g</sup>	0.22	1.18	2.24–2.35
<b>8e</b>	2.03	0.19	1.18	2.02–2.14
				2.24–2.32
				2.03–2.13
				2.24–2.33

<sup>a</sup> Measured in  $\text{CDCl}_3$ , with TMS as internal standard. <sup>b</sup> As a doublet, ca.  $J = 3.0$  Hz, for dienes; ca.  $J = 5.2$  Hz for complexes. <sup>c</sup> As a doublet,  $J = 3.5$  Hz, for diene **3a**; as a quartet,  $J = 7.3$  Hz, for diene **4a**, and as triplet,  $J = 7.7$  Hz, for diene **5a**; as a doublet, ca.  $J = 5.3$  Hz for complexes **6a–e**; as a quartet, ca.  $J = 6.4$  Hz for complexes **7a–e**; as a triplet, ca.  $J = 7.7$  Hz for complexes **8a–e**. <sup>d</sup> As a doublet, ca.  $J = 5.3$  Hz, for complexes **6a–e**; as a doublet, ca.  $J = 6.4$  Hz for complexes **7a–e**; as a multiplet for the methylene group of complexes **8a–e**. <sup>e</sup> ref<sup>14b</sup>. <sup>f</sup> Ref 28. <sup>g</sup> Signal overlapped by the multiplet of the methylene group.

$^1\text{H}$  NMR spectra of the series of complexes **6–8** show chemical shifts for all the vinylic protons that are largely shielded with respect to those of the precursor dienes (Table 2).<sup>26</sup> Protons H-6b and H-7b (the *in* protons) are more affected by the shielding effect of the tricarbonyliron complex than protons H-6a and H-7a (the *out* protons). This is due to the fact that the former are closer than the latter to the coordination sphere of the metal.<sup>26,27</sup> The larger upfield shielding effect on the protons H-7a and H-7b with respect to protons H-6 is a consequence of the larger delocalization of the nitrogen atom lone-pair with respect to the oxygen atom through the double bond, as also observed for the free-complex dienes **3–5**.<sup>14,28</sup> The signals of the vinylic protons were assigned by NOE experiments: For instance, for complex **6a**, irradiation of H-7a produced an enhancement of the

(22) Woodward, R. B. *J. Am. Chem. Soc.* **1942**, *64*, 72–75.(23) Lundquists, T. T.; Cais, M. *J. Org. Chem.* **1962**, *27*, 1167–1172.(24) For the full UV absorptions of dienes **3a**, **4a**, and **5a** and of complexes **6a**, **7a**, and **8a**, see Table 1 in Supporting Information.(25) (a) Pettit, R.; Emerson, G. F. *Adv. Organomet. Chem.* **1964**, *1*, 1–46. (b) Emme, I.; Labahn, T.; de Meijere, A. *Eur. J. Org. Chem.* **2006**, 399–404. (c) Docherty, G. F.; Knox, G. R.; Pauson, P. L. *J. Organomet. Chem.* **1998**, *568*, 287–290. (d) Reboul, V.; Guillou, C.; Tha, C. *Tetrahedron Lett.* **1999**, *40*, 8355–8358. (e) Christie, S. D. R.; Cummins, J.; Elsegood, M. R. J.; Dawson, G. *Synlett* **2009**, 257–259.(26) Danks, T. N.; Howells, M. E.; Ackland, M. J. *J. Organomet. Chem.* **1999**, *579*, 53–58.(27) (a) Chaudhury, S.; Donaldson, W. A.; Bennett, D. W.; Haworth, D. T.; Siddiquee, T. A.; Kloss, J. M. *J. Organomet. Chem.* **2004**, *689*, 1437–1443. (b) Ackland, M. J.; Danks, T. N.; Howells, M. E. *J. Chem. Soc., Perkin Trans. 1* **1998**, 813–817.(28) Benavides, A.; Martínez, R.; Jiménez-Vázquez, H. A.; Delgado, F.; Tamariz, J. *Heterocycles* **2001**, *55*, 469–485.





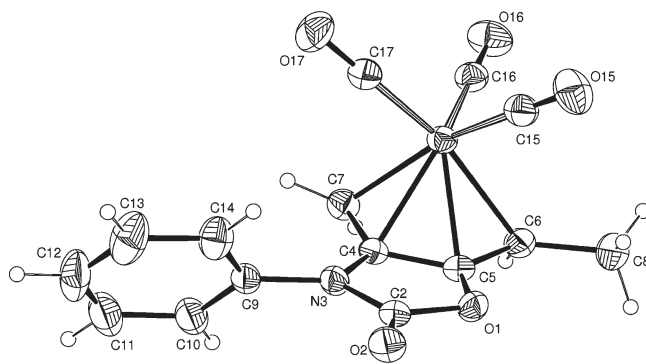
**Figure 1.** Molecular structure of **6c** (ellipsoids at 50% probability level). Select bond lengths (Å) and angles (deg): C(5)–C(6) 1.399(7), C(4)–C(7) 1.412(6), C(4)–C(5) 1.386(7), C(4)–Fe(1) 2.098(4), C(5)–Fe(1) 2.068(4), C(6)–Fe(1) 2.117(4), C(7)–Fe(1) 2.122(5); C(5)–C(4)–C(7) 120.0(4), C(4)–C(5)–C(6) 123.2(4), C(5)–C(4)–Fe(1) 69.4(3), C(7)–C(4)–Fe(1) 71.4(3), C(6)–C(5)–Fe(1) 72.4(3).

signals of proton H-7b (20%) and aryl protons (1.8%), while the irradiation of proton H-7b induced an enhancement of the signals of H-7a (24%) and H-6b (12%).

A strong shielding effect on the  $^{13}\text{C}$  NMR chemical shifts of the diene moiety is also observed due to the tricarbonyliron coordination, with respect to the noncomplexed dienes. This effect is much larger for the terminal carbons C-6 and C-7 of the diene (ca. 62 ppm) than that for the inner carbons C-4 and C-5 (ca. 27 ppm). This has been associated with a larger extent of hybridization change ( $\pi$  to  $\text{sp}^3$ ) of the terminal carbon atoms with respect to the inner carbons of the diene- $\text{Fe}(\text{CO})_3$  complex.<sup>29</sup>

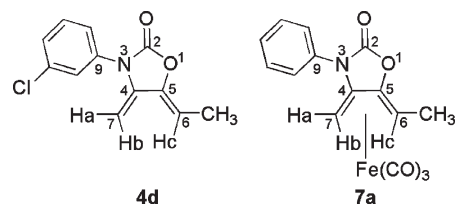
**X-ray Diffraction of  $\eta^4$ -Diene- $\text{Fe}(\text{CO})_3$  Complexes 6–8.** The structures of complexes **6–8** were unambiguously established by X-ray diffraction analysis, and interesting structural features can be extracted from them. The structure of complex **6c** shows a conformational preference for the coordination of fragment  $\text{Fe}(\text{CO})_3$  to the diene ligand, in which the iron atom lies over the plane of the butadiene ligand in a distorted trigonal square-pyramidal structure and is equidistant from each of the four carbon atoms ( $2.1 \pm 0.05$  Å) (Figure 1).<sup>30</sup> As expected,<sup>7b,25a,31</sup> two carbonyl ligands are pointing out from the metal to the C4 and C5 vertices, respectively, of the coordinated diene, and the third one is oriented to the center and at the opposite side of the diene moiety.

Comparison between the data of the X-ray structures of complex **7a** (Figure 2) and the analogue free diene **4d**<sup>14b</sup> provides the following features (Table 3): (a) Selected bond distances of the diene moiety indicate that, unlike free diene **4d**, where the inner C4–C5 bond is longer than the exocyclic double bonds (C4–C7 and C5–C6), in complex **7a** almost



**Figure 2.** Molecular structure of **7a** (ellipsoids at 30% probability level). Select bond lengths (Å) and angles (deg): C(4)–Fe(1) 2.083(3), C(5)–Fe(1) 2.078(3), C(6)–Fe(1) 2.151(3), C(7)–Fe(1) 2.109(3); C(5)–C(4)–N(3) 105.9(3), C(7)–C(4)–N(3) 132.7(3), N(3)–C(4)–Fe(1) 124.3(2), O(1)–C(5)–Fe(1) 124.1(2), C(4)–C(5)–O(1) 108.9(3).

**Table 3.** X-ray Selected Data of the Structures of Diene **4d** and  $\eta^4$ -Diene- $\text{Fe}(\text{CO})_3$  Complex **7a**



	<b>4d</b>	<b>7a</b>
Bond Distances (Å)		
C4–C5	1.44(1)	1.389(4)
C4–C7	1.34(1)	1.410(4)
C5–C6	1.28(1)	1.402(5)
Bond Angles (deg)		
C4–C5–C6	132.0(7)	123.5(3)
C5–C4–C7	128.7(8)	121.0(3)
C5–C6–Me	126.5(7)	121.5(3)
Dihedral Angles (deg)		
C4–C5–C6–Me	179.2	170.8
C7–C4–N3–C9	–4.0	9.4
C7–C4–N3–C2	178.7	–171.7
C6–C5–O–C2	177.1	174.4

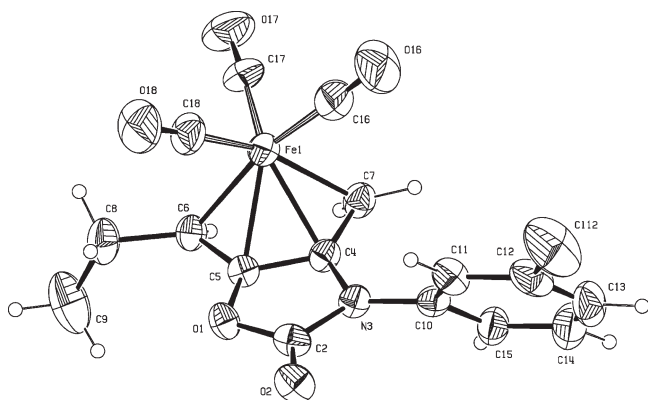
equalized C–C bond lengths within the coordinated diene ligand are observed (note: the inner C4–C5 bond is shorter than the exocyclic double bonds);<sup>32</sup> (b) selected bond angles of the dienic frame of **7a** show that there is a reduction of these angles with respect to the free diene **4d** (Table 3), which can be associated with the  $\pi$ -back-bonding effect of the metal that produces the hybridization at the carbon atoms of the vinylic double bonds to approach  $\text{sp}^3$ ; (c) the dihedral angle values in complex **7a** support the previous observation, since the  $\text{sp}^3$ -like hybridization of the carbon dienic frame should cause the substituents (methyl group and vinylic protons) to bend back from the metal (note: the value (170.8°) for the dihedral angle C4–C5–C6–Me indicates a nonplanarity of the methyl group with respect to the plane of the heterocycle, and the coordination generates a distortion of the coplanarity

(29) Retcofsky, H. L.; Frankel, E. N.; Gutowsky, H. S. *J. Am. Chem. Soc.* **1966**, *88*, 2710–2712.

(30) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.

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**Figure 3.** Molecular structure of **8d** (ellipsoids at 30% probability level). Select bond lengths (Å) and angles (deg): C(4)–Fe(1) 2.068(8), C(5)–Fe(1) 2.083(8), C(6)–Fe(1) 2.151(9), C(7)–Fe(1) 2.096(9); C(5)–C(4)–Fe(1) 70.9(6), C(7)–C(4)–Fe(1) 71.6(5), C(6)–C(5)–Fe(1) 73.2(5), C(4)–C(5)–Fe(1) 69.7(6), C(4)–C(7)–Fe(1) 69.4(5), C(5)–C(6)–Fe(1) 68.0(5), C(8)–C(6)–Fe(1) 125.4(6).

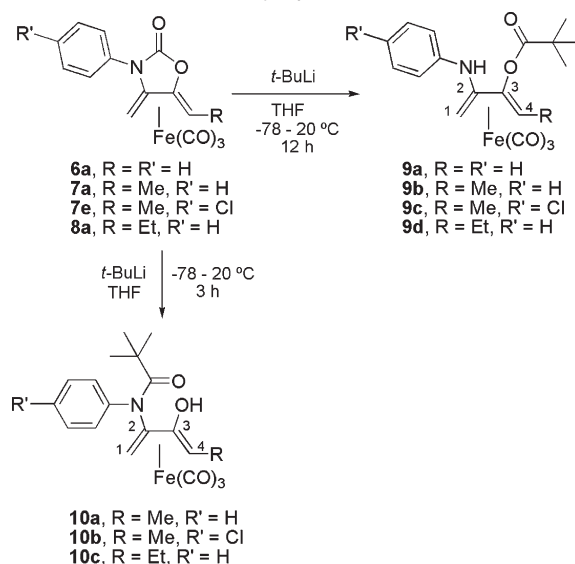
between the diene and the heterocycle, as suggested by the dihedral angles C7–C4–N3–C9 (9.4°) and C7–C4–N3–C2 (–171.7°); (d) although in both cases, diene **4d** and complex **7a**, the aromatic ring is almost orthogonal with respect to the heterocycle plane; in **7a** the aromatic ring is also bending back from the side of the Fe(CO)<sub>3</sub> coordination.

Similar structural features are observed for the ethyl-substituted diene **8d**, whose X-ray structure is shown in Figure 3.

**Reactivity of Complexes 6–8. Preparation of Enamine-Enol Ester Fe(CO)<sub>3</sub> Complexes 9a–9d and Enamido-Enol Fe(CO)<sub>3</sub> Complexes 10–11.** Although the tricarbonyliron group has been useful as a stabilizing group for dienes and related unsaturated systems,<sup>1a,33</sup> the Fe(CO)<sub>3</sub> group can assist the functionalization of the diene in the  $\eta^4$ -coordination complex through a variety of reactions with a high regio- and stereoselectivity.<sup>8–12,34</sup> Therefore, we decided to explore the reactivity and selectivity of complexes **6–8** in such reactions. Thus, following the acylation protocol described by Franck–Newmann for the synthesis of optically active alcohols,<sup>35</sup> diene **7a** was submitted to similar Friedel–Crafts conditions (AcCl, AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0–20 °C).<sup>36</sup> However, the reaction gave rise to the full recovery of the starting material, even if the acylation agent (Ac<sub>2</sub>O) and the catalyst (BF<sub>3</sub>·Et<sub>2</sub>O) were changed. Upon increasing the reaction temperature, decomposition of the complex was also observed.

Following the known protocol of deprotonation and electrophilation of diene Fe(CO)<sub>3</sub> complexes,<sup>11b</sup> compound **7a** was treated with LDA at low temperature (–78 °C) and methyl iodide or *p*-nitrobenzaldehyde was added to trap the likely preformed carbanion. However, starting material was recovered. The inductive electron donor effect of the diene Fe(CO)<sub>3</sub> scaffold may be the cause of the low acidity of the protons of the methyl group grafted to the diene.<sup>25a</sup>

**Scheme 3.** Reactivity of Diene Fe(CO)<sub>3</sub> Complexes **6–8** with *t*-BuLi



**Table 4.** Preparation of  $\eta^4$ -Diene Fe(CO)<sub>3</sub> Complexes **9a–d**, **10a–c**, and **11a–f**

entry	diene complex	nucleophile	method <sup>a</sup>	product	mp (°C)	yield (%) <sup>b</sup>
1	<b>6a</b>	<i>t</i> -BuLi	A	<b>9a</b>	oil	35
2	<b>7a</b>	<i>t</i> -BuLi	A	<b>9b</b>	69–70	45
3	<b>7e</b>	<i>t</i> -BuLi	A	<b>9c</b>	59–60	40
4	<b>8a</b>	<i>t</i> -BuLi	A	<b>9d</b>	99–100	20
5	<b>7b</b>	<i>t</i> -BuLi	B	<b>10a</b>	89–90	35
6	<b>7e</b>	<i>t</i> -BuLi	B	<b>10b</b>	109–110	35
7	<b>8a</b>	<i>t</i> -BuLi	B	<b>10c</b>	110–111	40
8	<b>6a</b>	MeLi	A	<b>11a</b>	97–98	20
9	<b>6a</b>	<i>n</i> -BuLi	A	<b>11b</b>	oil	40
10	<b>6a</b>	MeLi	B	<b>11a</b>	97–98	5
11	<b>6a</b>	<i>n</i> -BuLi	B	<b>11b</b>	oil	30
12	<b>7a</b>	MeLi	A	<b>11c</b>	115–116	25
13	<b>7a</b>	EtLi	A	<b>11d</b>	oil	25
14	<b>7a</b>	<i>n</i> -BuLi	A	<b>11e</b>	oil	60
15	<b>7a</b>	<i>s</i> -BuLi	A	<b>11f</b>	oil	40
16	<b>7a</b>	MeLi	B	<b>11c</b>	115–116	5
17	<b>7a</b>	EtLi	B	<b>11d</b>	oil	5
18	<b>7a</b>	<i>n</i> -BuLi	B	<b>11e</b>	oil	40
19	<b>7a</b>	<i>s</i> -BuLi	B	<b>11f</b>	oil	30

<sup>a</sup> Method A: Alkylolithium (1.0 mol equiv), THF, N<sub>2</sub> atm, –70 °C to rt (3 h), then stirring for 12 h. Method B: Alkylolithium (1.0 mol equiv), THF, N<sub>2</sub> atm, –70 °C to –10 °C, then stirring for 3 h. <sup>b</sup> Calculated after column chromatography.

The origin of this stability of the complex may also be due to the electron-releasing effect of the heteroatoms of the fused heterocycle toward the diene Fe(CO)<sub>3</sub> coordination. Therefore, this effect would inhibit the electron delocalization of the heteroatom lone-pairs toward the carbonyl group of the oxazolidinone ring of complexes **6–8**. To gain more insight about this hypothesis, the reactivity of strong hard nucleophiles, such as *tert*-butyllithium, was evaluated. Indeed, complex **7a** underwent the attack of the nucleophilic species to provide the enamine-enol ester complex **9b** as the major product (Scheme 3), and nonreacted starting material was recovered (Table 4). The reaction was extended to complexes **6a**, **7e**, and **8a**, observing similar results (Scheme 3). Thus, when they were submitted to similar reaction conditions, complexes **9a**, **9c**, and **9d**, were isolated, respectively, in low to moderate yields (Table 4, entries 1–4).

(33) (a) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463–469. (b) Birch, A. J.; Kelly, L. F. *J. Organomet. Chem.* **1985**, *285*, 267–280.

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(35) (a) Franck-Newmann, M.; Chemla, P.; Martina, D. *Synlett* **1990**, 641–642. (b) Wasicak, J. T.; Craig, R. A.; Henry, R.; Dasgupta, B.; Li, H.; Donaldson, W. A. *Tetrahedron* **1997**, *53*, 4185–4198.

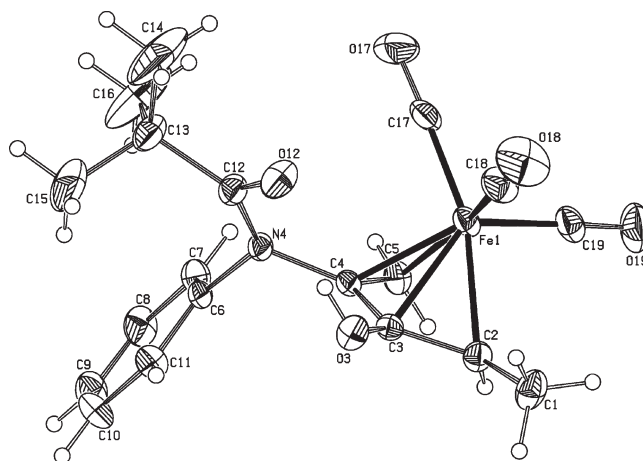
(36) Tagliaferri, E.; Campiche, P.; Roulet, R.; Gabioud, R.; Vogel, P.; Chapuis, G. *Helv. Chim. Acta* **1985**, *68*, 126–134.

The structure of these complexes was established by spectroscopy. For example, the IR spectrum of **9b** shows a band at  $3388\text{ cm}^{-1}$ , which corresponds to the stretching vibration of the N–H bond, as well as the strong bands between  $2046$  and  $1944\text{ cm}^{-1}$  corresponding to the stretching frequencies of the carbonyl groups of the  $\text{Fe}(\text{CO})_3$  moiety, and at  $1748\text{ cm}^{-1}$  a strong-intensity band appears due to the C=O stretching mode of the ester group. In comparison with the chemical shifts of the corresponding protons of complex **7a** (Table 2), in the  $^1\text{H}$  NMR spectrum of complex **9b**, besides the presence of the signal of the *tert*-butyl group as a singlet at 1.38 ppm, the signals due to the *gem*-vinyl protons H-1a (2.21 ppm) and H-1b (0.29 ppm) are shifted slightly to low field, and proton H-4 is shifted to high field (1.09 ppm). In the  $^{13}\text{C}$  NMR spectrum of complex **9b**, the signal of the carbon atom of the carbonyl group is largely deshielded to 176.6 ppm, with respect to the chemical shift of the carbonyl group of the cyclic carbamate (154.6 ppm) of **7a**, which indicates that the latter was converted to an ester group. The assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were supported by 2D (HMQC, HMBC) and NOE experiments.

Interestingly, in contrast with the previous protocol (method A), in which the reaction mixture was slowly warmed (about 3 h) to room temperature and then stirred for 12 h, a different product was furnished when the reaction with **7b** was carried out by adding the lithium reagent at  $-78\text{ }^\circ\text{C}$ , followed by rapidly increasing the temperature to  $-10\text{ }^\circ\text{C}$ , stirring for 3 h, and quenching the reaction mixture by water addition (method B). This product corresponded to enamido-enol  $\text{Fe}(\text{CO})_3$  **10a**, and it was obtained as a single product (Scheme 3). Similar behavior was observed by reacting substrates **7e** and **8a**, giving conjugated enamido-enols **10b** and **10c**, respectively (Table 4, entries 5–7).

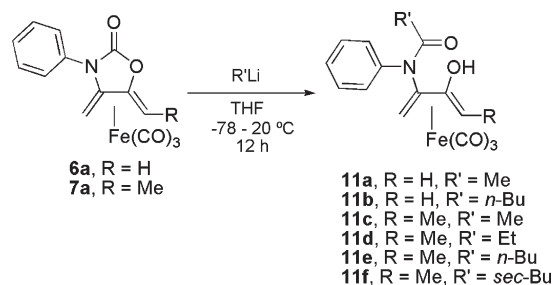
These results suggest that in the formation of complexes **10a–c** the least stable product was captured, whereas in the formation of **9b** by warming to room temperature and maintaining the reaction for 12 h, the most stable product, **9**, was isolated.

The structure of these complexes was also established by spectroscopy. For example, the IR spectrum of **10a** shows a broad band at  $3440\text{ cm}^{-1}$ , which corresponds to the stretching vibration of the O–H bond. At  $1617$  and  $1591\text{ cm}^{-1}$  two medium-intensity bands appear due to the C=O stretching mode of the amide group, and the strong bands corresponding to the stretching frequencies of the carbonyl groups of the  $\text{Fe}(\text{CO})_3$  moiety are also found. In the  $^1\text{H}$  NMR spectrum of this complex, the singlet of the *tert*-butyl group is shielded to 1.07 ppm, as well as the signals due to the *gem*-vinyl protons H-1a (1.40 ppm), H-1b ( $-0.52$  ppm), and H-4 (0.90 ppm) with respect to the chemical shifts of the corresponding protons of complex **9b** (*vide supra*). In the  $^{13}\text{C}$  NMR spectrum of complex **10a**, the signal of the carbon atom of the amide group is more deshielded (183.4 ppm) than the chemical shift of the carbonyl group of the ester group (176.6 ppm) of **9b**, which suggests that the lone-pair of the nitrogen atom is not coplanar to the  $\pi$  orbital of the carbonyl group of the amide in the former complex. Interestingly, a similar but strong downfield shift (129.5 ppm) is observed for the carbon atom C-2, the base of the nitrogen atom of the enamido moiety. In contrast, the carbon atom C-3, the base of the oxygen atom of the enol moiety, is shifted to high field (97.5 ppm) with respect to the same carbon atoms of the enamine (114.1 ppm) and the ester (111.3 ppm) moieties of complex **9b**. This spectroscopic analysis of the structure of



**Figure 4.** Molecular structure of **10b** (ellipsoids with 30% probability level). Select bond lengths (Å) and angles (deg): C(2)–Fe(1) 2.123(4), C(3)–Fe(1) 2.118(3), C(4)–Fe(1) 2.049(3), C(5)–Fe(1) 2.059(4), C(4)–N(4) 1.452(5); C(3)–C(2)–Fe(1) 70.3(2), C(1)–C(2)–Fe(1) 124.6(3), O(3)–C(3)–C(4) 122.4(3), O(3)–C(3)–Fe(1) 126.6(3), C(4)–C(3)–Fe(1) 67.5(2), C(2)–C(3)–Fe(1) C(5)–C(4)–N(4) 118.9(3), N(4)–C(4)–Fe(1) 129.3(3).

**Scheme 4. Reactivity of Diene  $\text{Fe}(\text{CO})_3$  Complexes **6a** and **7a** with Alkyl Lithium Reagents**



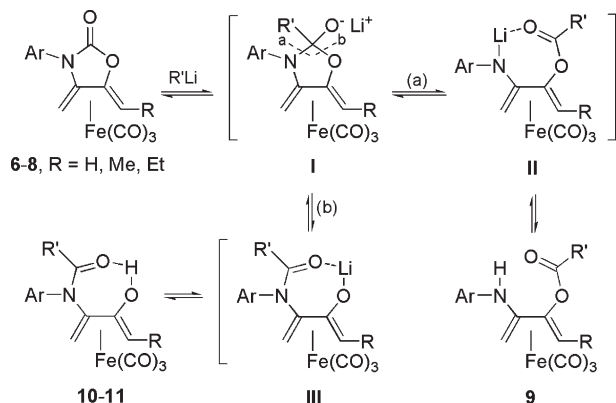
**10b** was supported by the measurement of its X-ray diffraction structure (Figure 4). The latter reveals that  $\text{Fe}(\text{CO})_3$  binds to the  $\eta^4$ -diene ligand, in which the conformation of the carbonyl group of the amide is oriented to the hydroxyl group, being stabilized by an intramolecular hydrogen bonding. The crystal lattice exhibited static disorder due to the random presence of the two possible conformers of the *tert*-butyl group among different unit cells.

Compounds **9a–d** and **10a–c** represent a novel example of stabilization of highly reactive and unstable conjugated enamino-enol esters and enamido-enols by coordination to  $\text{Fe}(\text{CO})_3$ . Actually, conjugated enols stabilized by complexing to the  $\text{Fe}(\text{CO})_3$  group have been previously reported in the literature.<sup>37</sup> However, to the best of our knowledge, this is the first time that a stabilized enol conjugated to an enamido group is described.

With the aim of further evaluating the regioselectivity in the opening of the oxazolidin-2-one ring by alkyllithium additions, methyl lithium, ethyl lithium, *n*-butyllithium, or *sec*-butyllithium was added to **6a** and **7a** (Scheme 4). Table 4 summarizes the results of these additions under both reaction conditions. Unexpectedly, the addition of methyl lithium to **6a** under both methods provided a single product, which corresponded to the enamido-enol complex **11a** (Table 4, entries 8 and 10). Analogous results were

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**Scheme 5. Selectivity in Carbamate Ring-Opening of Diene Fe(CO)<sub>3</sub> Complexes 6–8 by Additions of Alkyl lithium Reagent**

observed with the addition of *n*-butyllithium, to yield only complex **11b** (Table 4, entries 9 and 11). Similarly, when the series of alkyl lithium reagents were reacted with complex **7a**, the additions turned out to give only the enamido-enol complexes **11c–f** (Table 4, entries 12–19). In all cases, method A was more efficient than method B for the conversion, giving higher yields.

These results suggest that the enamido-enol complexes **11a–f** are both the kinetic and the most stable opened-ring products. This can be explained by the fact that, after addition of the alkyl lithium to the carbonyl group of the cyclic carbamate, the opening pathway (a) of the ring in species **I** leads to the lithium enamide **II**, which is a stronger base (less stable) than enolate **III**. This is in turn formed by the opening pathway (b) of the ring in species **I** (Scheme 5). Hence, in the case of the addition of these alkyl lithium reagents, the unstable intermediate **II** cannot be reached. All attempts to isolate the enamine-enol ester products, such as **9**, from the addition of the alkyl lithium reagents were unsuccessful, since increasing the reaction temperatures above room temperature showed the same enamido-enol complexes or decomposition of the starting material. In contrast, it is likely that in the case of the addition of *tert*-butyllithium, intermediates **II** and **III** have similar stabilities.

### Conclusions

We have synthesized a series of new  $\eta^4$ -diene-Fe(CO)<sub>3</sub> complexes **6a–e**, **7a–e**, and **8a–e** derived from the novel *exo*-2-oxazolidinone dienes. The complexation of the latter was carried out by thermal treatment with diiron nonacarbonyl to afford the corresponding complexes as crystal solids. The X-ray diffraction analysis of complexes **6c**, **7a**, and **8d** did not reveal any unusual structural features, in agreement with the structures of common diene-iron complexes. Evaluation of the reactivity of these complexes under acylation or base-promoted electrophilation conditions provided evidence of the high stability of these complexes. Because of this stability, the carbonyl group of the cyclic carbamate resulted in the reactive electrophilic center of the molecule, to the extent that it underwent the addition of alkyl lithium reagents. The outcome of the latter allowed for the isolation of either stable and unprecedented conjugated enamine-enol ester Fe(CO)<sub>3</sub> complexes **9a–d**, which proved to be the thermodynamic products, or the less stable enamido-enol Fe(CO)<sub>3</sub> complexes **10a–c** and **11a–f**.

### Experimental Section

**General Procedures and Instrumentation.** Melting points (uncorrected) were determined with a Fisher-Johns capillary melting point apparatus. IR spectra were recorded on a Perkin-Elmer 2000 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian Mercury (300 MHz) and Varian VNMR System (500 MHz) NMR instruments, with CDCl<sub>3</sub> as the solvent and TMS as internal standard. High-resolution mass spectra (HRMS) were obtained, in electron impact (EI) (70 eV) mode, on a Jeol JSM-GCMate II spectrometer. X-ray crystallographic structures were obtained on Siemens P4 and Oxford XcaliburS diffractometers. UV spectral data were recorded on a Bausch & Lomb Spectronic 2000. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). Analytical TLC was carried out using E. Merck silica gel 60 F<sub>254</sub> coated 0.25 plates, visualized by a long- and short-wavelength UV lamp. Flash column chromatography was performed over Natland International Co. silica gel (230–400 mesh). All air- and moisture-sensitive reactions were carried out under nitrogen using oven-dried glassware. Benzene and THF were freshly distilled over sodium, and methylene chloride and ethyl acetate over calcium hydride, prior to use. All other reagents were used without further purification. Dienes **3a–e**, **4a–e**, and **5a–e** were prepared as reported.<sup>14b,c,28</sup>

**General Method for the Preparation of Complexes 6a–e, 7a–e, and 8a–e.** A mixture of Fe<sub>2</sub>(CO)<sub>9</sub> (8.02 mmol, 3 equiv), the corresponding diene, **3a–e**, **4a–e**, or **5a–e** (2.67 mmol, 1 equiv), and freshly dried benzene (5 mL) were placed in a 25 mL two-necked, round-bottomed flask (equipped with a reflux condenser and a rubber septum), and the mixture was stirred and heated at reflux for 3 h under nitrogen atmosphere. Upon cooling, the reaction mixture was filtered over Celite, and the solvent was removed under vacuum. The crude product was purified by column chromatography over silica gel impregnated with triethylamine (10%) in hexane (hexane/EtOAc, 9:1), to give complexes **6a–e**, **7a–e**, or **8a–e**.

**Tricarbonyl- $\eta^4$ -[4,5-dimethylene-3-phenyl-1,3-oxazolidin-2-one]iron(0) (**6a**).** Following the general method, with 0.50 g of **3a** and 2.92 g of Fe<sub>2</sub>(CO)<sub>9</sub>, 0.655 g (75%) of **6a** was obtained as a yellow-greenish solid: mp 119–120 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 2052, 1980, 1962 [Fe(CO)<sub>3</sub>], 1764 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.33 (d, *J* = 5.2 Hz, 1H, H-7b), 0.51 (d, *J* = 5.4 Hz, 1H, H-6b), 2.17 (d, *J* = 5.2 Hz, 1H, H-7a), 2.59 (d, *J* = 5.4 Hz, 1H, H-6a), 7.41–7.57 (m, 5H, Ph-H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  19.6 (C-7), 21.8 (C-6), 111.0 (C-4), 122.3 (C-5), 125.0 (C-9), 128.3 (C-11), 129.5 (C-10), 132.5 (C-8), 154.2 (C-2), 206–209 [Fe(CO)<sub>3</sub>]; MS (70 eV) *m/z* 327 (M<sup>+</sup>, 2), 299 (6), 271 (30), 243 (100), 189 (13), 172 (14), 91 (18), 77 (16), 56 (50), 51 (15). Anal. Calcd for C<sub>14</sub>H<sub>9</sub>NO<sub>5</sub>Fe: C, 51.41; H, 2.77; N, 4.28. Found: C, 51.50; H, 2.82; N, 4.23.

**Tricarbonyl- $\eta^4$ -[4,5-dimethylene-3-(2-methylphenyl)-1,3-oxazolidin-2-one]iron(0) (**6b**).** Following the general method, with 0.537 g of **3b** and 2.92 g of Fe<sub>2</sub>(CO)<sub>9</sub>, 0.382 g (42%) of **6b** as a mixture of atropoisomers (66:34) was obtained as yellow crystals: mp 158–160 °C; FT-IR  $\nu_{\text{max}}$  (film) 2039, 1963 [Fe(CO)<sub>3</sub>], 1780 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.30 (d, *J* = 5.0 Hz, 1H, H-7b), 0.50 (d, *J* = 5.1 Hz, 1H, H-6b), 1.90 (d, *J* = 5.0 Hz, 1H, H-7a), 2.38 (s, 3H, CH<sub>3</sub>-Ar), 2.59 (d, *J* = 5.1 Hz, 1H, H-6a), 7.23–7.54 (m, 4H, H-10, H-11, H-12, H-13); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  17.1 (CH<sub>3</sub>-Ar), 19.4 (C-7), 22.1 (C-6), 111.7 (C-4), 123.0 (C-5), 127.5, 127.6, 130.1, 131.0 (C-8), 131.7, 135.7 (C-9), 155.0 (C-2), 206–208 [Fe(CO)<sub>3</sub>]. Signals attributed to the minor isomer: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.35 (d, *J* = 5.0 Hz, 1H, H-7b), 1.94 (d, *J* = 5.0 Hz, 1H, H-7a), 2.25 (s, 3H, CH<sub>3</sub>-Ar); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  18.3 (CH<sub>3</sub>-Ar), 20.2 (C-7), 21.9 (C-6), 111.8 (C-4), 123.9 (C-5), 126.8, 127.1, 129.4, 132.1, 136.3, 153.7 (C-2). Anal. Calcd for C<sub>15</sub>H<sub>11</sub>NO<sub>5</sub>Fe: C, 52.82; H, 3.25; N, 4.11. Found: C, 52.91; H, 3.43; N, 4.06.



**Tricarbonyl- $\eta^4$ -[4,5-dimethylene-3-(4-methylphenyl)-1,3-oxazolidin-2-one]iron(0) (6c).** Following the general method, with 0.537 g of **3c** and 2.92 g of  $\text{Fe}_2(\text{CO})_9$ , 0.482 g (53%) of **6c** was obtained as a yellow-greenish solid: mp 123–124 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 2054, 1980, 1964  $[\text{Fe}(\text{CO})_3]$ , 1783 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.30 (d,  $J = 5.2$  Hz, 1H, H-7b), 0.50 (d,  $J = 5.4$  Hz, 1H, H-6b), 2.13 (d,  $J = 5.2$  Hz, 1H, H-7a), 2.41 (s, 3H,  $\text{CH}_3$ -Ar), 2.58 (d,  $J = 5.4$  Hz, 1H, H-6a), 7.29–7.39 (m, 4H, H-9, H-10);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  20.2 (C-7), 21.2 ( $\text{CH}_3$ -Ar), 22.2 (C-6), 111.6 (C-4), 122.7 (C-5), 125.3 (C-9), 130.1 (C-8), 130.5 (C-10), 139.0 (C-11), 154.9 (C-2), 206–209  $[\text{Fe}(\text{CO})_3]$ ; MS (70 eV)  $m/z$  341 ( $\text{M}^+$ , 1), 283 (2), 267 (14), 237 (1), 193 (3), 161 (33), 146 (35), 133 (10), 132 (100), 91 (77), 65 (33), 38 (13). Anal. Calcd for  $\text{C}_{15}\text{H}_{11}\text{NO}_5\text{Fe}$ : C, 52.82; H, 3.25; N, 4.11. Found: C, 52.97; H, 3.16; N, 4.19.

**Tricarbonyl- $\eta^4$ -[3-(3-chlorophenyl)-4,5-dimethylene-1,3-oxazolidin-2-one]iron(0) (6d).** Following the general method, with 0.591 g of **3d** and 2.92 g of  $\text{Fe}_2(\text{CO})_9$ , 0.366 g (38%) of **6d** was obtained as a yellow solid: mp 110–111 °C; FT-IR  $\nu_{\text{max}}$  (film) 2049, 1976  $[\text{Fe}(\text{CO})_3]$ , 1782 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.34 (d,  $J = 3.0$  Hz, 1H, H-7b), 0.52 (d,  $J = 3.4$  Hz, 1H, H-6b), 2.17 (d,  $J = 3.0$  Hz, 1H, H-7a), 2.60 (d,  $J = 3.4$  Hz, 1H, H-6a), 7.36–7.83 (m, 4H, H-9, H-11, H-12, H-13);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  20.0 (C-7), 22.4 (C-6), 110.7 (C-4), 122.8 (C-5), 123.4 (C-13), 125.5 (C-9), 129.0 (C-11), 139.0 (C-12), 133.9 (C-8), 135.5 (C-10), 154.2 (C-2), 206–209  $[\text{Fe}(\text{CO})_3]$ ; MS (70 eV)  $m/z$  361 ( $\text{M}^+$ , 2), 333 (7), 305 (55), 277 (100), 241 (38), 197 (40), 167 (17), 142 (28), 91 (19), 84 (41). Anal. Calcd for  $\text{C}_{14}\text{H}_8\text{ClNO}_5\text{Fe}$ : C, 46.51; H, 2.23; N, 3.87. Found: C, 46.75; H, 2.19; N, 3.70.

**Tricarbonyl- $\eta^4$ -[3-(4-chlorophenyl)-4,5-dimethylene-1,3-oxazolidin-2-one]iron(0) (6e).** Following the general method, with 0.591 g of **3e** and 2.92 g of  $\text{Fe}_2(\text{CO})_9$ , 0.386 g (40%) of **6e** was obtained as a yellow solid: mp 107–109 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 2054, 1976  $[\text{Fe}(\text{CO})_3]$ , 1786 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.32 (d,  $J = 5.3$  Hz, 1H, H-7b), 0.51 (d,  $J = 5.4$  Hz, 1H, H-6b), 2.13 (d,  $J = 5.3$  Hz, 1H, H-7a), 2.60 (d,  $J = 5.4$  Hz, 1H, H-6a), 7.41–7.52 (m, 4H, H-9, H-10);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  19.9 (C-7), 22.4 (C-6), 110.8 (C-4), 122.8 (C-5), 126.6 (C-9), 130.2 (C-10), 131.3 (C-8), 134.6 (C-11), 154.4 (C-2), 206–209  $[\text{Fe}(\text{CO})_3]$ ; MS (70 eV)  $m/z$  361 ( $\text{M}^+$ , 2), 333 (5), 305 (35), 277 (100), 241 (6), 197 (11), 167 (11), 142 (11), 91 (12), 84 (27), 56 (41). Anal. Calcd for  $\text{C}_{14}\text{H}_8\text{ClNO}_5\text{Fe}$ : C, 46.51; H, 2.23; N, 3.87. Found: C, 46.34; H, 2.12; N, 3.86.

**Tricarbonyl- $\eta^4$ -[(Z)-5-ethylidene-4-methylene-3-phenyl-1,3-oxazolidin-2-one]iron(0) (7a).** Following the general method, with 0.537 g of **4a** and 2.92 g of  $\text{Fe}_2(\text{CO})_9$ , 0.783 g (86%) of **7a** was obtained as yellow crystals: mp 163–164 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 2050, 1970, 1964  $[\text{Fe}(\text{CO})_3]$ , 1782 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.20 (d,  $J = 5.2$  Hz, 1H, H-7b), 1.27 (q,  $J = 6.4$  Hz, 1H, H-6), 1.83 (d,  $J = 6.4$  Hz, 3H,  $\text{CH}_3$ ), 2.05 (d,  $J = 5.2$  Hz, 1H, H-7a), 7.39–7.57 (m, 5H, H-9, H-10, H-11);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9 ( $\text{CH}_3$ ), 18.7 (C-7), 38.8 (C-6), 107.9 (C-4), 123.3 (C-5), 125.4 (C-9), 128.7 (C-11), 129.9 (C-10), 132.9 (C-8), 154.6 (C-2), 206–209  $[\text{Fe}(\text{CO})_3]$ ; MS (70 eV)  $m/z$  201 ( $\text{M}^+$ , 100), 186 (1), 156 (21), 142 (3), 118 (93), 104 (15), 77 (73), 65 (6). Anal. Calcd for  $\text{C}_{15}\text{H}_{11}\text{NO}_5\text{Fe}$ : C, 52.82; H, 3.25; N, 4.11. Found: C, 52.65; H, 3.05; N, 4.03.

**Tricarbonyl- $\eta^4$ -[(Z)-5-ethylidene-4-methylene-3-(2-methylphenyl)-1,3-oxazolidin-2-one]iron(0) (7b).** Following the general method, with 0.574 g of **4b** and 2.92 g of  $\text{Fe}_2(\text{CO})_9$ , 0.407 g (43%) of **7b** as a mixture of atropoisomers (63:37) was obtained as a yellow solid: mp 158–160 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 2049, 1973  $[\text{Fe}(\text{CO})_3]$ , 1766 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.19 (d,  $J = 5.1$  Hz, 1H, H-7b), 1.27 (q,  $J = 6.4$  Hz, 1H, H-6), 1.78 (d,  $J = 5.1$  Hz, 1H, H-7a), 1.84 (d,  $J = 6.4$  Hz, 3H,  $\text{CH}_3$ ), 2.37 (s, 3H,  $\text{CH}_3$ -Ar), 7.26–7.43 (m, 4H, H-10, H-11, H-12, H-13);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  13.8 ( $\text{CH}_3$ ), 18.7 (C-7), 38.7 (C-6), 107.9 (C-4), 123.3 (C-5), 124.3, 128.3, 128.7, 129.8, 131.1 (C-8), 132.8 (C-9), 154.6 (C-2), 208–209  $[\text{Fe}(\text{CO})_3]$ . Signals attributed to the minor isomer:  $^1\text{H}$

NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.23 (d,  $J = 5.2$  Hz, 1H, H-7b), 1.28 (q,  $J = 6.4$  Hz, 1H, H-6), 1.82 (d,  $J = 5.2$  Hz, 1H, H-7a), 1.83 (d,  $J = 6.4$  Hz, 3H,  $\text{CH}_3$ ), 2.25 (s, 3H,  $\text{CH}_3$ -Ar). Anal. Calcd for  $\text{C}_{16}\text{H}_{13}\text{NO}_5\text{Fe}$ : C, 54.11; H, 3.69; N, 3.94. Found: C, 54.11; H, 3.71; N, 4.02.

**Tricarbonyl- $\eta^4$ -[(Z)-5-ethylidene-4-methylene-3-(4-methylphenyl)-1,3-oxazolidin-2-one]iron(0) (7c).** Following the general method, with 0.574 g of **4c** and 2.92 g of  $\text{Fe}_2(\text{CO})_9$ , 0.597 g (63%) of **7c** was obtained as a yellow solid: mp 102–103 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 2042, 1980, 1960  $[\text{Fe}(\text{CO})_3]$ , 1770 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.19 (d,  $J = 5.2$  Hz, 1H, H-7b), 1.27 (q,  $J = 6.5$  Hz, 1H, H-6), 1.83 (d,  $J = 6.5$  Hz, 3H,  $\text{CH}_3$ ), 2.02 (d,  $J = 5.2$  Hz, 1H, H-7a), 2.41 (s, 3H,  $\text{CH}_3$ -Ar), 7.25–7.39 (m, 4H, H-9, H-10);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  13.8 ( $\text{CH}_3$ ), 18.6 (C-7), 21.1 ( $\text{CH}_3$ -Ar), 38.7 (C-6), 108.1 (C-4), 123.2 (C-5), 125.3 (C-9), 130.1 (C-8), 130.5 (C-10), 138.9 (C-11), 154.8 (C-2), 206–209  $[\text{Fe}(\text{CO})_3]$ ; MS (70 eV)  $m/z$  355 ( $\text{M}^+$ , 2), 327 (3), 299 (26), 271 (100), 227 (1), 215 (4), 174 (16), 91 (11), 84 (5), 56 (15). Anal. Calcd for  $\text{C}_{16}\text{H}_{13}\text{NO}_5\text{Fe}$ : C, 54.11; H, 3.69; N, 3.94. Found: C, 54.23; H, 3.83; N, 3.96.

**Tricarbonyl- $\eta^4$ -[(Z)-3-(3-chlorophenyl)-5-ethylidene-4-methylene-1,3-oxazolidin-2-one]iron(0) (7d).** Following the general method, with 0.629 g of **4d** and 2.92 g of  $\text{Fe}_2(\text{CO})_9$ , 0.481 g (48%) of **7d** was obtained as yellow crystals: mp 161–162 °C; FT-IR  $\nu_{\text{max}}$  (film) 2036, 1968  $[\text{Fe}(\text{CO})_3]$ , 1782 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.22 (d,  $J = 5.3$  Hz, 1H, H-7b), 1.29 (q,  $J = 6.5$  Hz, 1H, H-6), 1.83 (d,  $J = 6.5$  Hz, 3H,  $\text{CH}_3$ ), 2.07 (d,  $J = 5.3$  Hz, 1H, H-7a), 7.35–7.66 (m, 4H, H-9, H-11, H-12, H-13);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  13.8 (C-7), 18.7 (C-6), 39.0 (C-4), 107.3 (C-5), 123.3 (C-5), 123.4 (C-13), 125.5 (C-9), 128.9 (C-11), 130.9 (C-12), 134.0 (C-8), 135.9 (C-10), 154.2 (C-2), 206–209  $[\text{Fe}(\text{CO})_3]$ ; MS (70 eV)  $m/z$  375 ( $\text{M}^+$ , 2), 347 (5), 319 (49), 291 (100), 255 (27), 211 (20), 155 (15), 111 (10), 84 (15). Anal. Calcd for  $\text{C}_{15}\text{H}_8\text{ClNO}_5\text{Fe}$ : C, 47.97; H, 2.68; N, 3.73. Found: C, 47.77; H, 2.74; N, 3.76.

**Tricarbonyl- $\eta^4$ -[(Z)-3-(4-chlorophenyl)-5-ethylidene-4-methylene-1,3-oxazolidin-2-one]iron(0) (7e).** Following the general method, with 0.629 g of **4e** and 2.92 g of  $\text{Fe}_2(\text{CO})_9$ , 0.36 g (36%) of **7e** was obtained as yellow crystals: mp 105–106 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 2050, 1972  $[\text{Fe}(\text{CO})_3]$ , 1780 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.21 (d,  $J = 5.3$  Hz, 1H, H-7b), 1.29 (q,  $J = 6.4$  Hz, 1H, H-6), 1.83 (d,  $J = 6.4$  Hz, 3H,  $\text{CH}_3$ ), 2.02 (d,  $J = 5.3$  Hz, 1H, H-7a), 7.43–7.50 (m, 4H, H-9, H-10);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  13.8 ( $\text{CH}_3$ ), 18.5 (C-7), 39.0 (C-6), 107.4 (C-4), 123.3 (C-5), 126.6 (C-9), 130.1 (C-10), 131.4 (C-8), 134.5 (C-11), 154.3 (C-2), 206–209  $[\text{Fe}(\text{CO})_3]$ ; MS (70 eV)  $m/z$  375 ( $\text{M}^+$ , 2), 347 (4), 319 (30), 291 (100), 255 (3), 211 (4), 207 (11), 155 (6), 111 (9), 91 (10), 84 (18), 56 (34). Anal. Calcd for  $\text{C}_{15}\text{H}_{10}\text{ClNO}_5\text{Fe}$ : C, 47.97; H, 2.68; N, 3.73. Found: C, 48.09; H, 2.88; N, 3.72.

**Tricarbonyl- $\eta^4$ -[(Z)-4-methylene-3-phenyl-5-propylidene-1,3-oxazolidin-2-one]iron(0) (8a).** Following the general method, with 0.574 g of **5a** and 2.92 g of  $\text{Fe}_2(\text{CO})_9$ , 0.549 g (58%) of **8a** was obtained as a yellow solid: mp 126–127 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 2044, 1980, 1956  $[\text{Fe}(\text{CO})_3]$ , 1756 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.20 (d,  $J = 5.2$  Hz, 1H, H-7b), 1.17 (dd,  $J = 7.6$ , 6.8 Hz, 1H, H-6), 1.26 (t,  $J = 7.4$  Hz, 3H,  $\text{CH}_3\text{CH}_2$ ), 2.06 (d,  $J = 5.2$  Hz, 1H, H-7a), 2.03–2.13 (m, 1H,  $\text{CH}_3\text{CH}_2$ ), 2.24–3.34 (m, 1H,  $\text{CH}_3\text{CH}_2$ ), 7.38–7.59 (m, 5H, H-9, H-10, H-11);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  15.9 ( $\text{CH}_3\text{CH}_2$ ), 18.8 (C-7), 22.5 ( $\text{CH}_3\text{CH}_2$ ), 47.6 (C-6), 107.9 (C-4), 122.5 (C-5), 125.4 (C-9), 128.7 (C-11), 129.9 (C-10), 132.9 (C-8), 154.7 (C-2), 207–209  $[\text{Fe}(\text{CO})_3]$ ; MS (70 eV)  $m/z$  215 ( $\text{M}^+$ , 65), 170 (5), 156 (4), 129 (4), 118 (100), 77 (48), 51 (20). Anal. Calcd for  $\text{C}_{16}\text{H}_{13}\text{NO}_5\text{Fe}$ : C, 54.11; H, 3.69; N, 3.94. Found: C, 53.90; H, 4.00; N, 3.85.

**Tricarbonyl- $\eta^4$ -[(Z)-4-methylene-3-(2-methylphenyl)-5-propylidene-1,3-oxazolidin-2-one]iron(0) (8b).** Following the general method, with 0.611 g of **5b** and 2.92 g of  $\text{Fe}_2(\text{CO})_9$ , 0.472 g (48%) of **8b** as a mixture of atropoisomers (62:38) was obtained as yellow crystals: mp 113–115 °C; FT-IR  $\nu_{\text{max}}$  (film) 2047,

1970 [Fe(CO)<sub>3</sub>], 1782 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.19 (d, *J* = 5.1 Hz, 1H, H-7b), 1.14–1.23 (m, 1H, H-6), 1.27 (t, *J* = 7.3 Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>), 1.80 (d, *J* = 5.1 Hz, 1H, H-7a), 2.01–2.19 (m, 1H, CH<sub>3</sub>CH<sub>2</sub>), 2.22–2.42 (m, 1H, CH<sub>3</sub>CH<sub>2</sub>), 2.38 (s, 3H, CH<sub>3</sub>-Ar), 7.26–7.43 (m, 4H, H-10, H-11, H-12, H-13); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 15.9 (CH<sub>3</sub>CH<sub>2</sub>), 18.0 (CH<sub>3</sub>-Ar), 18.1 (C-7), 22.6 (CH<sub>3</sub>CH<sub>2</sub>), 47.5 (C-6), 108.3 (C-4), 122.9 (C-5), 127.5, 127.9, 130.1, 131.1 (C-8), 131.6, 135.8 (C-9), 154.7 (C-2), 207–209 [Fe(CO)<sub>3</sub>]. Signals attributed to the minor isomer: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.23 (d, *J* = 5.1 Hz, 1H, H-7b), 1.84 (d, *J* = 5.1 Hz, 1H, H-7a), 2.25 (s, 3H, CH<sub>3</sub>-Ar); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 18.9 (C-7), 22.6 (CH<sub>3</sub>CH<sub>2</sub>), 47.3 (C-6), 126.9, 127.1, 129.4, 131.0 (C-8), 132.1 (C-9). Anal. Calcd for C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub>Fe: C, 55.31; H, 4.10; N, 3.79. Found: C, 55.46; H, 4.22; N, 3.76.

**Tricarbonyl-η<sup>4</sup>-(*Z*)-4-methylene-3-(4-methylphenyl)-5-propylidene-1,3-oxazolidin-2-oneiron(0) (8c).** Following the general method, with 0.611 g of **5c** and 2.92 g of Fe<sub>2</sub>(CO)<sub>9</sub>, 0.512 g (52%) of **8c** was obtained as a yellow crystalline solid: mp 113–114 °C; FT-IR ν<sub>max</sub> (film) 2042, 1981, 1951 [Fe(CO)<sub>3</sub>], 1778 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.18 (d, *J* = 5.2 Hz, 1H, H-7b), 1.15 (dd, *J* = 7.9, 6.5 Hz, 1H, H-6), 1.25 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>), 2.03 (d, *J* = 5.2 Hz, 1H, H-7a), 2.02–2.13 (m, 1H, CH<sub>3</sub>CH<sub>2</sub>), 2.24–2.35 (m, 1H, CH<sub>3</sub>CH<sub>2</sub>), 2.41 (s, 3H, CH<sub>3</sub>-Ar), 7.28–7.37 (m, 4H, H-9, H-10); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 15.9 (CH<sub>3</sub>CH<sub>2</sub>), 18.7 (C-7), 21.2 (CH<sub>3</sub>-Ar), 22.5 (CH<sub>3</sub>CH<sub>2</sub>), 47.5 (C-6), 108.2 (C-4), 122.5 (C-5), 125.4 (C-9), 130.1 (C-8), 130.5 (C-10), 138.9 (C-11), 154.9 (C-2), 207–209 [Fe(CO)<sub>3</sub>]; MS (70 eV): *m/z* 369 (M<sup>+</sup>, 1), 341 (3), 313 (24), 285 (100), 229 (5), 132 (9), 91 (10), 56 (12). Anal. Calcd for C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub>Fe: C, 55.31; H, 4.10; N, 3.79. Found: C, 55.40; H, 4.16; N, 3.74.

**Tricarbonyl-η<sup>4</sup>-(*Z*)-3-(3-chlorophenyl)-4-methylene-5-propylidene-1,3-oxazolidin-2-oneiron(0) (8d).** Following the general method, with 0.666 g of **5d** and 2.92 g of Fe<sub>2</sub>(CO)<sub>9</sub>, 0.613 g (59%) of **8d** was obtained as a pale yellow solid: mp 121–122 °C; FT-IR ν<sub>max</sub> (KBr) 2044, 1972, 1956 [Fe(CO)<sub>3</sub>], 1770 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.22 (d, *J* = 5.2 Hz, 1H, H-7b), 1.18 (dd, *J* = 7.9, 6.5 Hz, 1H, H-6), 1.26 (t, *J* = 7.3 Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>), 2.02–2.14 (m, 2H, H-7a and CH<sub>3</sub>CH<sub>2</sub>), 2.24–2.32 (m, 1H, CH<sub>3</sub>CH<sub>2</sub>), 7.38–7.43 (m, 2H, H-11 and H-13), 7.45–7.48 (m, 1H, H-12), 7.52–7.53 (m, 1H, H-9); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 15.9 (CH<sub>3</sub>CH<sub>2</sub>), 18.8 (C-7), 22.5 (CH<sub>3</sub>CH<sub>2</sub>), 47.7 (C-6), 107.3 (C-4), 122.6 (C-5), 123.4 (C-13), 125.5 (C-9), 128.9 (C-11), 130.9 (C-12), 134.0 (C-8), 135.5 (C-10), 154.2 (C-2), 207–209 [Fe(CO)<sub>3</sub>]; MS (70 eV) *m/z* 389 (M<sup>+</sup>, 1), 361 (4), 333 (42), 305 (100), 269 (29), 223 (13), 167 (16), 111 (9), 84 (19), 56 (17). Anal. Calcd for C<sub>16</sub>H<sub>12</sub>ClNO<sub>5</sub>Fe: C, 49.32; H, 3.10; N, 3.59. Found: C, 49.11; H, 3.22; N, 3.60.

**Tricarbonyl-η<sup>4</sup>-(*Z*)-3-(4-chlorophenyl)-4-methylene-5-propylidene-1,3-oxazolidin-2-oneiron(0) (8e).** Following the general method, with 0.629 g of **5e** and 2.92 g of Fe<sub>2</sub>(CO)<sub>9</sub>, 0.449 g (48%) of **8e** was obtained as a pale yellow solid: mp 127–128 °C; FT-IR ν<sub>max</sub> (KBr) 2046, 1984, 1960 [Fe(CO)<sub>3</sub>], 1766 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.19 (d, *J* = 5.2 Hz, 1H, H-7b), 1.18 (dd, *J* = 7.8, 6.6 Hz, 1H, H-6), 1.30 (t, *J* = 7.3 Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>), 2.03 (d, *J* = 5.2 Hz, 1H, H-7a), 2.03–2.13 (m, 1H, CH<sub>3</sub>CH<sub>2</sub>), 2.24–2.33 (m, 1H, CH<sub>3</sub>CH<sub>2</sub>), 7.42–7.47 (m, 2H, H-9), 7.40–7.52 (m, 2H, H-10); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 15.9 (CH<sub>3</sub>CH<sub>2</sub>), 18.6 (C-7), 22.5 (CH<sub>3</sub>CH<sub>2</sub>), 47.7 (C-6), 107.5 (C-4), 122.6 (C-5), 126.6 (C-9), 130.2 (C-10), 131.4 (C-8), 134.6 (C-11), 154.8 (C-2), 207–209 [Fe(CO)<sub>3</sub>]. Anal. Calcd for C<sub>16</sub>H<sub>12</sub>ClNO<sub>5</sub>Fe: C, 49.33; H, 3.10; N, 3.59. Found: C, 49.45; H, 3.03; N, 3.60.

**General Methods for the Reaction of Complexes 6a, 7a, 7e, and 8a with *t*-BuLi.** **Method A.** To a solution of the corresponding complexes **6a**, **7a**, **7e**, or **8a** (0.6 mmol) in 5 mL of dry THF at –70 °C was slowly added *t*-BuLi (0.6 mmol, 1.7 M) under nitrogen atmosphere. The mixture was allowed to reach room temperature (~3 h) and stirred for 12 h. At this point, the solvent

was removed and the dark brown residue was dissolved in EtOAc (10 mL) and filtered over alumina. The solvent was removed under vacuum, and the crude product was purified by column chromatography over silica gel (hexane/EtOAc, 9:1), to afford complexes **9a–d**.

**Method B.** To a solution of the corresponding complex **7a**, **7e**, or **8a** (0.6 mmol) in 5 mL of dry THF at –70 °C was slowly added *t*-BuLi (0.6 mmol, 1.7 M) under nitrogen atmosphere. The mixture was allowed to reach –10 °C (~3 h). At this point, the solvent was removed and the dark brown residue was dissolved in EtOAc (10 mL) and filtered over alumina. The solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel (hexane/EtOAc, 9:1), to afford complexes **10a–c**.

**Tricarbonyl-η<sup>4</sup>-(3-(phenylamino)-2-(pivaloyloxy)buta-1,3-diene)iron(0) (9a).** Following method A with **6a**, complex **9a** (35%) was obtained as a brown oil: FT-IR ν<sub>max</sub> (KBr) 3420 (NH), 2046, 1967, [Fe(CO)<sub>3</sub>], 1750 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.26 (d, *J* = 4.8 Hz, 1H, H-4b), 0.45 (d, *J* = 4.8 Hz, 1H, H-1a), 1.35 (s, 9H, H-11), 1.94 (d, *J* = 4.8 Hz, 3H, H-4a), 2.28 (d, *J* = 4.8 Hz, 1H, H-1b), 5.51 (s, 1H, NH), 7.03 (t, *J* = 7.8 Hz, 1H, H-8), 7.11 (d, *J* = 7.8 Hz, 2H, H-6), 7.29 (d, *J* = 7.8 Hz, 2H, H-7); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 27.0 (C-11), 31.1 (C-4), 32.2 (C-1), 39.4 (C-10), 110.8 (C-3), 117.8 (C-2), 120.5 (C-6), 123.4 (C-8), 129.3 (C-7), 140.6 (C-5), 177.4 (CO); HRMS (EI) calcd for C<sub>18</sub>H<sub>19</sub>FeNO<sub>5</sub>[M]<sup>+</sup> 385.0616, found 385.0615.

**Tricarbonyl-η<sup>4</sup>-(*Z*)-2-(phenylamino)-3-(pivaloyloxy)penta-1,3-dieneiron(0) (9b).** Following method A with **7a**, complex **9b** (45%) was obtained as a brown solid: mp 69–70 °C; FT-IR ν<sub>max</sub> (KBr) 3388 (NH), 2046, 2033, 1969, 1944 [Fe(CO)<sub>3</sub>], 1748 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.29 (d, *J* = 4.5 Hz, 1H, H-1b), 1.09 (q, *J* = 6.0 Hz, 1H, H-4), 1.38 (s, 9H, H-11), 1.47 (d, *J* = 6.0 Hz, 3H, CH<sub>3</sub>), 2.21 (d, *J* = 4.5 Hz, 1H, H-1a), 5.34 (s, 1H, NH), 6.97–7.08 (m, 3H, H-6, H-8), 7.26–7.30 (m, 2H, H-7); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 14.8 (CH<sub>3</sub>), 27.1 (C-11), 30.4 (C-1), 39.3 (C-10), 46.9 (C-4), 111.3 (C-3), 114.1 (C-2), 120.0 (C-6), 122.7 (C-8), 129.3 (C-7), 141.1 (C-5), 176.6 (CO); HRMS (EI) calcd for C<sub>18</sub>H<sub>21</sub>NO<sub>4</sub>Fe [M – 28]<sup>+</sup> 371.0820, found 371.0814.

**Tricarbonyl-η<sup>4</sup>-(*Z*)-2-(4-chlorophenylamino)-3-(pivaloyloxy)penta-1,3-dieneiron(0) (9c).** Following method A with **7e**, complex **9c** (30%) was obtained as a brown solid: mp 59–60 °C; FT-IR ν<sub>max</sub> (KBr) 3415 (NH), 2043, 1979, 1958, [Fe(CO)<sub>3</sub>], 1755 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.27 (d, *J* = 4.5 Hz, 1H, H-1b), 0.88 (q, *J* = 6.3 Hz, 1H, H-4), 1.38 (s, 9H, H-11), 1.46 (d, *J* = 6.3 Hz, 3H, CH<sub>3</sub>), 2.13 (d, *J* = 4.5 Hz, 1H, H-1a), 5.32 (s, 1H, NH), 6.90 (d, *J* = 8.4 Hz, 2H, H-6), 7.24 (d, *J* = 8.4 Hz, 2H, H-7); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 14.8 (CH<sub>3</sub>), 27.1 (C-11), 31.5 (C-1), 39.3 (C-10), 47.0 (C-4), 112.9 (C-3), 113.6 (C-2), 121.0 (C-6), 127.5 (C-8), 129.3 (C-7), 140.0 (C-5), 176.6 (CO); HRMS (EI) calcd for C<sub>19</sub>H<sub>20</sub>ClNO<sub>5</sub>Fe [M]<sup>+</sup> 433.0379, found 433.0374.

**Tricarbonyl-η<sup>4</sup>-(*Z*)-2-(phenylamino)-3-(pivaloyloxy)hexa-1,3-dieneiron(0) (9d).** Following method A with **8a**, complex **9d** (40%) was obtained as a brown solid: mp 99–100 °C; FT-IR ν<sub>max</sub> (KBr) 3396 (NH), 2037, 1959, [Fe(CO)<sub>3</sub>], 1748 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.29 (d, *J* = 4.5 Hz, 1H, H-1b), 0.87 (t, *J* = 6.9 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.90–0.96 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.09 (t, *J* = 7.3 Hz, 1H, H-4), 1.38 (s, 9H, H-11), 2.23 (d, *J* = 4.5 Hz, 1H, H-1a), 5.34 (s, 1H, NH), 6.97–7.08 (m, 3H, H-6, H-8), 7.24–7.29 (m, 2H, H-7); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 15.7 (C-4), 23.0 (CH<sub>2</sub>CH<sub>3</sub>), 27.1 (C-11), 30.7 (C-1), 39.3 (C-10), 55.9 (CH<sub>2</sub>CH<sub>3</sub>), 112.2 (C-3), 114.2 (C-2), 120.0 (C-6), 122.6 (C-8), 129.3 (C-7), 141.2 (C-5), 176.6 (CO); HRMS (EI) calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>5</sub>Fe [M]<sup>+</sup> 413.0926, found 413.0928.

**Tricarbonyl-η<sup>4</sup>-(*Z*)-3-hydroxy-2-(*N*-phenylpivalamido)penta-1,3-dieneiron(0) (10a).** Following method B with **7a**, complex **10a** (35%) was obtained as a brown solid: mp 89–99 °C; FT-IR ν<sub>max</sub> (KBr) 3448 (OH), 2040, 1979, 1951 [Fe(CO)<sub>3</sub>], 1617, 1591 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ –0.52 (d, *J* = 4.2 Hz, 1H, H-1b), 0.90 (q, *J* = 6.0 Hz, 1H, H-4), 1.07 (s, 9H, H-11),



1.40 (d,  $J = 4.2$  Hz 3H, H-1a), 1.59 (d,  $J = 6.0$  Hz, 3H, CH<sub>3</sub>), 7.34–7.40 (m, 5H, H-6, H-7, H-8), 8.20 (s, 1H, OH); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  14.3 (CH<sub>3</sub>), 29.4 (C-11), 31.9 (C-1), 42.6 (C-10), 52.5 (C-4), 97.5 (C-3), 129.5 (C-2, C-6), 129.4 (C-8), 130.4 (C-7), 144.0 (C-5), 183.4 (CO); HRMS (EI) calcd for C<sub>18</sub>H<sub>21</sub>NO<sub>4</sub>Fe [M – 28]<sup>+</sup> 371.0820, found 371.0815.

**Tricarbonyl- $\eta^4$ [(*Z*)-3-hydroxy-2-(*N*-phenylpivalamido)hexa-1,3-diene]iron(0) (10b).** Following method B with **7e**, complex **10b** (35%) was obtained as a brown solid: mp 110–111 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 3448 (OH), 2043, 1964, [Fe(CO)<sub>3</sub>], 1630, 1593 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  –0.53 (d,  $J = 4.5$  Hz, 1H, H-1b), 0.78–0.87 (m, 3H, H-4, CH<sub>2</sub>CH<sub>3</sub>), 1.07 (s, 9H, H-11), 1.12 (t,  $J = 7.3$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.41 (d,  $J = 4.5$  Hz, 1H, H-1a), 7.34–7.43 (m, 5H, H-6, H-7, H-8), 8.20 (s, 1H, OH); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  15.8 (CH<sub>2</sub>CH<sub>3</sub>), 22.8 (C-4), 29.4 (C-11), 32.0 (C-1), 42.6 (C-10), 61.4 (CH<sub>2</sub>CH<sub>3</sub>), 97.4 (C-3), 128.5 (C-6), 128.9 (C-2), 129.0 (C-8), 130.1 (C-7), 143.7 (C-5), 183.1 (CO); HRMS (EI) calcd for C<sub>18</sub>H<sub>23</sub>NO<sub>3</sub>Fe [M – 56]<sup>+</sup> 357.1027, found 357.1015.

**Tricarbonyl- $\eta^4$ [(*Z*)-2-(*N*-4-chlorophenylpivalamido)-3-hydroxyhexa-1,3-diene]iron(0) (10c).** Following method B with **8a**, complex **10c** (35%) was obtained as a brown solid: mp 109–110 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 3448 (OH), 2044, 1972, 1958, [Fe(CO)<sub>3</sub>], 1620, 1595 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  –0.52 (d,  $J = 4.2$  Hz, 1H, H-1b), 0.90 (q,  $J = 6.0$  Hz, 1H, H-4), 1.09 (s, 9H, H-11), 1.33 (d,  $J = 4.2$  Hz 1H, H-1a), 1.59 (d,  $J = 6.0$  Hz, 3H, CH<sub>3</sub>), 7.31 (d,  $J = 8.4$  Hz, 2H, H-6), 7.42 (d,  $J = 8.4$  Hz, 2H, H-7), 8.17 (s, 1H, OH); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  14.5 (CH<sub>3</sub>), 29.7 (C-11), 31.9 (C-1), 42.8 (C-10), 52.9 (C-4), 97.6 (C-3), 105.0 (C-2), 129.7 (C-6), 131.8 (C-7), 135.5 (C-8), 142.5 (C-5), 183.4 (CO).

**General Methods for the Reaction of Complexes 6a and 7a with Alkyl Lithium Reagents. Method A.** To a solution of the corresponding complex **6a** or **7a** (0.6 mmol) in 5 mL of dry THF at –70 °C was slowly added RLi (R = Me, Et, *n*-Bu, or *s*-Bu) (0.6 mmol) under nitrogen atmosphere. The mixture was allowed to reach room temperature (~3 h) and stirred for 12 h. At this point, the solvent was removed and the dark brown residue was dissolved in EtOAc (10 mL) and filtered over alumina. The solvent was removed under vacuum, and the crude product was purified by column chromatography over silica gel (hexane/EtOAc, 99:1), to afford complexes **11a–f**.

**Method B.** To a solution of complex **7a** (0.6 mmol) in 5 mL of dry THF at –70 °C was slowly added RLi (R = Me, Et, *n*-Bu, or *s*-Bu) (0.6 mmol) under nitrogen atmosphere. The mixture was allowed to reach –10 °C (~3 h). At this point, the solvent was removed and the dark brown residue was dissolved in EtOAc (10 mL) and filtered over alumina. The solvent was removed under vacuum, and the crude product was purified by column chromatography over silica gel (hexane/EtOAc, 99:1), to afford complexes **11a–f**.

**Tricarbonyl- $\eta^4$ [(*Z*)-3-hydroxy-2-(*N*-phenylethanamido)buta-1,3-diene]iron(0) (11a).** Starting with **6a**, complex **11a** was obtained at 20% by following method A and at 5% by following method B, both as a brown solid: mp 97–98 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 3449 (OH), 2048, 1968 [Fe(CO)<sub>3</sub>], 1635 (C=O), cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  –0.51 (d,  $J = 4.2$  Hz, 1H, H-1b), 0.13 (d,  $J = 4.2$  Hz, 1H, H-4b), 1.31 (d,  $J = 4.2$  Hz, 3H, H-1a), 2.08 (s, 3H, CH<sub>3</sub>CO), 2.24 (d,  $J = 4.2$  Hz, 1H, H-4a), 7.26–7.48 (m, 5H, H-6, H-7, H-8), 8.50 (s, 1H, OH); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  25.1 (C-10), 33.4 (C-1), 36.0 (C-4), 97.0 (C-3), 128.2 (C-6), 129.0 (C-8), 129.1 (C-2), 130.0 (C-7), 143.7 (C-5), 174.8 (CO); HRMS (EI) calcd for C<sub>14</sub>H<sub>13</sub>NO<sub>4</sub>Fe [M – 28]<sup>+</sup> 315.0194, found 315.0194.

**Tricarbonyl- $\eta^4$ [(*Z*)-3-hydroxy-2-(*N*-phenylpentanamido)buta-1,3-diene]iron(0) (11b).** Starting with **6a**, complex **11b** was obtained at 40% by following method A and at 30% by following method B, both as a brown oil: FT-IR  $\nu_{\text{max}}$  (KBr) 3451 (OH), 2048, 1964 [Fe(CO)<sub>3</sub>], 1634 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  –0.53 (d,  $J = 4.5$  Hz, 1H, H-1b), 0.13 (d,

$J = 4.2$  Hz, 1H, H-4b), 0.82 (t,  $J = 6.0$  Hz, 3H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CO), 0.88–0.92 (m, 3H, H-1a, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CO), 1.58–1.64 (m, 2H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CO), 2.14–2.20 (m, 1H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CO), 2.24 (d,  $J = 4.2$  Hz, 1H, H-4a), 2.31–2.36 (m, 1H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CO), 7.27–7.49 (m, 5H, H-6, H-7, H-8), 8.53 (s, 1H, OH); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  13.6 (C-13), 22.1 (C-11), 27.4 (C-12), 33.8 (C-1), 36.0 (C-4), 36.3 (C-10), 97.2 (C-3), 128.4 (C-6), 128.9 (C-2), 129.0 (C-8), 130.0 (C-7), 143.3 (C-5), 177.7 (CO).

**Tricarbonyl- $\eta^4$ [(*Z*)-3-hydroxy-2-(*N*-phenylethanamido)penta-1,3-diene]iron(0) (11c).** Starting with **7a**, complex **11c** was obtained at 25% by following method A and at 5% by following method B, both as a brown solid: mp 115–116 °C; FT-IR  $\nu_{\text{max}}$  (KBr) 3449 (OH), 2045, 1957 [Fe(CO)<sub>3</sub>], 1636 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  –0.52 (d,  $J = 4.2$  Hz, 1H, H-1b), 0.90 (q,  $J = 6.0$  Hz, 1H, H-4), 1.33 (d,  $J = 4.2$  Hz, 1H, H-1a), 1.59 (d,  $J = 6.0$  Hz, 3H, CH<sub>3</sub>), 2.08 (s, 3H, CH<sub>3</sub>CO), 7.25–7.27 (m, 3H, H-6, H-7, H-8), 7.45–7.47 (m, 2H, H-7), 8.51 (s, 1H, OH); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  14.5 (CH<sub>3</sub>), 25.1 (CH<sub>3</sub>CO), 31.8 (C-1), 52.1 (C-4), 94.7 (C-3), 128.2 (C-2, C-6), 128.9 (C-8), 130.0 (C-7), 143.8 (C-5), 174.9 (CO); HRMS (EI) calcd for C<sub>14</sub>H<sub>15</sub>NO<sub>3</sub>Fe [M – 56]<sup>+</sup> 301.0401; found 301.0381.

**Tricarbonyl- $\eta^4$ [(*Z*)-3-hydroxy-2-(*N*-phenylpropanamido)penta-1,3-diene]iron(0) (11d).** Starting with **7a**, complex **11d** was obtained at 25% by following method A and at 5% by following method B, both as a brown oil: FT-IR  $\nu_{\text{max}}$  (KBr) 2043, 1965 [Fe(CO)<sub>3</sub>], 1714, 1668 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  –0.50 (d,  $J = 4.5$  Hz, 1H, H-1b), 0.78 (q,  $J = 6.3$  Hz, 1H, H-4), 1.12–1.17 (m, 4H, H-1a, CH<sub>3</sub>CH<sub>2</sub>CO), 1.54 (d,  $J = 6.3$  Hz, 3H, CH<sub>3</sub>), 4.09–4.15 (m, 1H, CH<sub>3</sub>CH<sub>2</sub>CO), 4.22–4.30 (m, 1H, CH<sub>3</sub>CH<sub>2</sub>CO), 7.14–7.34 (m, 5H, H-6, H-7, H-8), 8.31 (s, 1H, OH); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  14.2 (C-11), 14.4 (CH<sub>3</sub>), 31.5 (C-1), 33.5 (C-10), 51.5 (C-4), 96.2 (C-3), 127.5 (C-2), 127.7 (C-8), 129.0 (C-6), 129.1 (C-7), 142.9 (C-5), 176.9 (CO).

**Tricarbonyl- $\eta^4$ [(*Z*)-3-hydroxy-2-(*N*-phenylpentanamido)penta-1,3-diene]iron(0) (11e).** Starting with **7a**, complex **11e** was obtained at 60% by following method A and at 40% by following method B, both as a brown oil: FT-IR  $\nu_{\text{max}}$  (KBr) 2048, 1964 [Fe(CO)<sub>3</sub>], 1636, 1591 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  –0.50 (d,  $J = 4.5$  Hz, 1H, H-1b), 0.79–0.88 (m, 4H, H-1, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CO), 1.22–1.25 (m, 3H, H-1a, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CO), 1.59–1.67 (m, 5H, CH<sub>3</sub>, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CO), 2.15–2.23 (m, 1H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CO), 2.30–2.35 (m, 1H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CO), 7.27–7.48 (m, 5H, H-6, H-7, H-8), 8.54 (s, 1H, OH); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  13.6 (C-13), 14.9 (CH<sub>3</sub>), 22.0 (C-11), 27.5 (C-12), 31.8 (C-1), 36.3 (C-10), 52.1 (C-4), 94.9 (C-3), 128.4 (C-6), 128.7 (C-2), 128.8 (C-8), 129.9 (C-7), 143.4 (C-5), 177.6 (CO); HRMS (EI) calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>4</sub>Fe [M]<sup>+</sup> 399.0769, found 399.0755.

**Tricarbonyl- $\eta^4$ [(*Z*)-3-hydroxy-2-(2-methyl-*N*-phenylbutanamido)penta-1,3-diene]iron(0) (11f).** Starting with **7a**, complex **11f** was obtained at 40% by following method A and at 30% by following method B, both as a brown oil: FT-IR  $\nu_{\text{max}}$  (KBr) 2044, 1966 [Fe(CO)<sub>3</sub>], 1726 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  –0.51 (d,  $J = 4.2$  Hz, 1H, H-1b), 0.85–0.94 (m, 4H, H-4, CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CO), 1.05 (d,  $J = 6.3$  Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CO), 1.25 (d,  $J = 4.2$  Hz, 1H, H-1a), 1.32–1.43 (m, 1H, CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CO), 1.61 (d,  $J = 6.3$  Hz, 3H, CH<sub>3</sub>), 2.41–2.48 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CO), 7.21–7.47 (m, 5H, H-6, H-7, H-8), 8.50 (s, 1H, OH); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  9.3 (C-13), 14.3 (CH<sub>3</sub>), 19.2 (C-12), 28.1 (C-11), 31.8 (C-1), 40.8 (C-10), 52.2 (C-4), 94.9 (C-3), 128.1 (C-2), 128.3 (C-6), 128.8 (C-8), 129.0 (C-7), 143.5 (C-5), 181.4 (CO); HRMS (EI) calcd for C<sub>18</sub>H<sub>21</sub>NO<sub>4</sub>Fe [M – 28]<sup>+</sup> 371.0820, found 371.0820.

**Single-Crystal X-ray Crystallography.** A single crystal of compound **6c** was obtained by recrystallization from hexane/MeOH, 2:1, compound **7a** from hexane/C<sub>6</sub>H<sub>6</sub>, 2:1, compound **8d** from hexane/CH<sub>2</sub>Cl<sub>2</sub>, 9:1, and **10b** from CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:6, as yellow crystals. These were mounted on glass fibers. Crystallographic measurements were performed using Mo K $\alpha$  radiation (graphite crystal monochromator,  $\lambda = 71073$  Å) at room

temperature. Three standard reflections, which were monitored periodically, showed no change during data collection. Unit cell parameters were obtained from least-squares refinement of 26 reflections in the range  $2^\circ < 2\theta < 20^\circ$ . Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions and their atomic coordinates refined. Unit weights were used in the refinement. Details of data collection and refinement for these crystals are listed in Table 12 (Supporting Information) and CIF files, which include bond distances and angles, atomic coordinates, and anisotropic thermal parameters. Structures were solved using the SHELXTL,<sup>38</sup> SHELX97,<sup>39</sup> or SIR92<sup>40</sup> programs as implemented in the WinGX suite<sup>41</sup> and refined using SHELXTL or SHELX97 within WinGX, on a personal computer. In all cases ORTEP and packing diagrams were made with PLATON and ORTEP-3.<sup>42</sup>

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**Supporting Information Available:** Tables summarizing UV spectral data, melting points,  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of the complexes **6a–e**, **7a–e**, **8a–e**, **9a–d**, **10a–c**, and **11a–f**, including images of IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR (HMQC, HMBC, and NOE experiments), and mass spectra for most of the complexes. Crystallographic information for **6c**, **7a**, **8d**, and **10b** in cif format, including X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles. This material is available free of charge via the Internet at <http://pubs.acs.org> and from the Cambridge Crystallographic Data Centre (fax: +44-1223-336-003; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk); or <http://www.ccdc.cam.ac.uk>) as supplementary publication nos. CCDC 756198 (**6c**), CCDC 756199 (**7a**), CCDC 756200 (**8d**), and CCDC 756201 (**10b**).