

Synthesis and Stereochemistry of Half-Sandwich Alkynyl Amino Acidate Complexes of Rhodium(III), Iridium(III), and Ruthenium(II)

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The synthesis and characterization of optically active amino acidate alkynyl complexes of general formula $[(\eta^n\text{-ring})\text{M}(\text{aa})(\text{C}\equiv\text{CR})]$ ($(\eta^n\text{-ring})\text{M} = (\eta^5\text{-C}_5\text{Me}_5)\text{Rh}$; aa = L-proline (Pro); R = CMe₃ (**1**), SiMe₃ (**2**); $(\eta^n\text{-ring})\text{M} = (\eta^5\text{-C}_5\text{Me}_5)\text{Ir}$; aa = Pro; R = CMe₃ (**3**), SiMe₃ (**4**); aa = N-methyl-L-proline (MePro); R = CMe₃ (**5**), SiMe₃ (**6**); $(\eta^n\text{-ring})\text{M} = (\eta^6\text{-p-MeC}_6\text{H}_4\text{Pr})\text{-Ru}$; aa = L-alanine (Ala); R = Ph (**7**), CO₂Me (**8**); aa = Pro; R = Ph (**9**), CO₂Me (**10**)) are reported. The crystal structures of $(R_{\text{Ir}}, S_{\text{C}}, S_{\text{N}})\text{-3b}$ and $(S_{\text{Ir}}, S_{\text{C}}, S_{\text{N}})\text{-5}$ were determined by X-ray analysis. Both molecular structures exhibit analogous pseudo-octahedral arrangements of ligands around the chiral iridium center. The metals are η^5 -bonded to the pentamethylcyclopentadienyl group, linked in a chelate fashion through the aminic nitrogen and one of the carboxylate oxygens to the amino acidate, and bonded to a terminal almost linear *tert*-butyl ethynyl ligand. The configurational stability of the complexes was studied by circular dichroism and ¹H NMR spectroscopy. Complex **3b** epimerizes at Ir in CDCl₃ obeying a first-order rate law with $\Delta H^\ddagger = 91.4 \pm 3.4 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -20.8 \pm 10.8 \text{ J K}^{-1} \text{ mol}^{-1}$. The equilibrium constant for **3b** \rightleftharpoons **3a** is 2.70 ± 0.41 in methanol at 20 °C. A mechanistic interpretation of the epimerization process is proposed.

Introduction

Among biologically relevant molecules, α -amino acids are readily available and inexpensive ligands whose coordination behavior toward transition metal ions has been extensively studied.¹ The interest of the interaction between metal ions and α -amino acids or related molecules stems from the extremely important role that they play in a wide variety of biological processes² and from the possibility that they open as a source of chiral catalysts.³

In particular, in recent years, there have been reported several investigations on half-sandwich complexes of α -amino acids involving $(\eta^5\text{-C}_5\text{Me}_5)\text{M(III)}$ (M = Rh, Ir) or $(\eta^6\text{-arene})\text{M(II)}$ (M = Ru, Os) moieties.⁴ Most of them present "three-legged piano stool" geometries^{4a–x} and exhibit chirality in both the amino acid and the metal center.

On the other hand, transition metal alkynyls are a well-known type of organometallic compounds⁵ that have proved to be important species in organic and organometallic synthesis⁶ as well as a source of a large variety of complexes containing ligands formed from the transformation of alkynes.⁷

We have reported^{4f} the preparation of amino acidate complexes of Rh(III), Ir(III), and Ru(II) of formula $[(\eta^n\text{-ring})\text{M}(\text{aa})\text{Cl}]$ ($(\eta^n\text{-ring})\text{M} = (\eta^5\text{-C}_5\text{Me}_5)\text{Rh}$, $(\eta^5\text{-C}_5\text{Me}_5)\text{-Ir}$, or $(\eta^6\text{-p-MeC}_6\text{H}_4\text{Pr})\text{Ru}$), in which the amino acidate anions act as N,O chelate ligands, and found that in these compounds epimerization at the metal atom was fast even at temperatures below 0 °C.^{4e,8} Configurational stability at the metal is a desirable property for potential enantioselective catalysts. In this context, it has been found that in half-sandwich ruthenium compounds

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the exchange of the atom donor set N,O of coordinated salicylaldiminato or α -amino acidato anions for N,N chelate imine ligands substantially increases the configurational stability at the metal.⁹ To achieve a greater configurational stability, an alternative approach applicable to $[(\eta^n\text{-ring})\text{M}(\text{aa})\text{Cl}]$ complexes would be the exchange of the chloride by other auxiliary ligands such as η^1 -alkynyl anions.

Following our studies on transition metal complexes with chiral metal centers,^{4f,s,t,x,9b,c,10} in this paper we report the synthesis and characterization of pseudo-octahedral alkynyl complexes with α -amino acidate ligands of general formula $[(\eta^n\text{-ring})\text{M}(\text{aa})(\text{C}\equiv\text{CR})]$ ($(\eta^n\text{-ring})\text{M} = (\eta^5\text{-C}_5\text{Me}_5)\text{Rh}$, $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}$, or $(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}$). The absolute configuration of these complexes is established on the basis of X-ray diffraction studies, ¹H NMR measurements, and CD spectroscopy. The configurational stability at the metal is also studied.

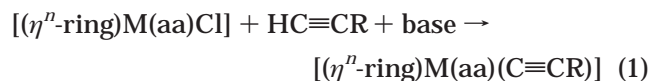
Part of this work has been previously communicated.¹¹

Results and Discussion

Synthesis of $[(\eta^n\text{-ring})\text{M}(\text{aa})(\text{C}\equiv\text{CR})]$ Complexes.

The α -amino acidate chloride compounds^{4e,f,8} $[(\eta^n\text{-ring})\text{M}(\text{aa})\text{Cl}]$ ($(\eta^n\text{-ring})\text{M} = (\eta^5\text{-C}_5\text{Me}_5)\text{Rh}$; aa = L-proline (Pro); $(\eta^n\text{-ring})\text{M} = (\eta^5\text{-C}_5\text{Me}_5)\text{Ir}$; aa = Pro, *N*-methyl-L-proline (MePro); $(\eta^n\text{-ring})\text{M} = (\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}$;

aa = L-alaninate (Ala), Pro) reacted with terminal alkynes $\text{HC}\equiv\text{CR}$ (R = CMe₃, SiMe₃, Ph, CO₂Me) in basic media (KOH or NEt₃), affording the corresponding alkynyl compounds $[(\eta^n\text{-ring})\text{M}(\text{aa})(\text{C}\equiv\text{CR})]$ (eq 1).



complex	$(\eta^n\text{-ring})\text{M}$	aa	R
1	$(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}$	Pro	CMe ₃
2	$(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}$	Pro	SiMe ₃
3	$(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}$	Pro	CMe ₃
4	$(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}$	Pro	SiMe ₃
5	$(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}$	MePro	CMe ₃
6	$(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}$	MePro	SiMe ₃
7	$(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}$	Ala	Ph
8	$(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}$	Ala	CO ₂ Me
9	$(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}$	Pro	Ph
10	$(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}$	Pro	CO ₂ Me

In the preparation of the rhodium derivatives **1** and **2**, KOH has to be used as base. In this respect, it is interesting to note that the reaction of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{Ala})\text{Cl}]$ with the terminal alkynes $\text{HC}\equiv\text{CR}$ (R = Ph, *p*-tolyl) in the presence of NEt₃ afforded trisubstituted cyclobutadiene complexes whose formation involved alkyne trimerization.^{4t}

For complexes **1–4** and **7** the formation of the two possible epimers at metal¹² has been spectroscopically observed, but the *N*-methyl proline derivatives **5** and **6** as well as the ruthenium compounds **8–10** were isolated as a single diastereomer since their NMR spectra showed a single set of sharp resonances. In this context, it has been pointed out that, in related $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}$ systems, only one diastereomer was detected for *N,N*-disubstituted amino acidates (as it is the case of compounds **5** and **6**),^{4q} but as far as we know such stereoselectivity has not been previously reported for related alaninate or proline derivatives.^{4e,f}

The reaction of formation of the iridium compounds **3–6** was monitored by ¹H NMR. The measurements revealed that the rate of formation of the complexes was relatively slow (for example, conversions of 37% and 48% were achieved after 15 h of reaction for complexes **5** and **6**, respectively) and that the observed diastereomeric composition of the products was the same at different conversions.

The complexes were characterized by analytical and spectroscopic techniques including the crystal structure determination by diffractometric means of one diastereomer of compounds **3** (**3b**) and **5** (see below). The

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(11) Carmona, D.; Lahoz, F. J.; Atencio, R.; Oro, L. A.; Lamata, M. P.; San José, E. *Tetrahedron: Asymmetry* **1993**, *4*, 1425. In this work, the relative thermodynamic stability in solution for complexes **3a** and **3b** was erroneously established.

(12) Complexes **1–4** and **7** were isolated with a diastereomeric excess of 24, 8, 50, 38, and 40%, respectively, according to ¹H NMR measurements in CDCl₃. The diastereomeric composition was established by accurate integration of corresponding ¹H NMR signals. Error limits on each integer are estimated as ± 2 .

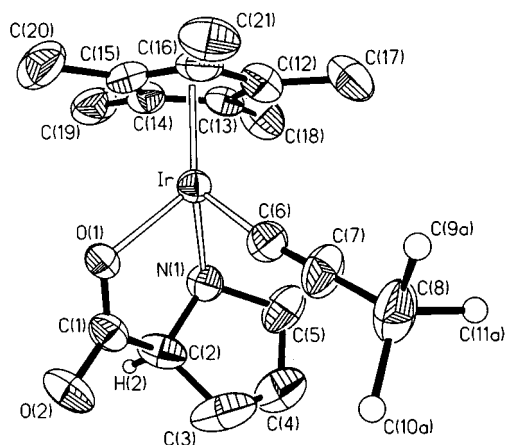


Figure 1. Molecular structure of $R_{Ir}, S_{C}, S_N-[(\eta^5-C_5Me_5)Ir-(Pro)(C\equiv CMe_3)]$ (**3b**) showing the atom-numbering scheme used. Hydrogen atoms bonded to the chiral centers N(1) and C(2) have also been represented (H(1) hidden by N(1)).

IR spectra showed bands at ca. 1600 ($\nu(CO)$)^{2b,13} and 3100 cm^{-1} ($\nu(NH)$)¹⁴ that indicated a N,O chelating nature for the amino acidate anion. A strong vibration between 2030 and 2115 cm^{-1} ($\nu(C\equiv C)$)¹⁵ in the IR, peaks at ca. 1.1 (CMe₃), 0.0 (SiMe₃), 3.6 (CO₂Me), or 7.1 (Ph) ppm in the ¹H NMR spectra, and two resonances between 80 and 124 ppm in the ¹³C NMR spectra confirmed the presence of the alkynyl ligand.

Molecular Structures of $R_{Ir}, S_{C}, S_N-[(\eta^5-C_5Me_5)Ir-(Pro)(C\equiv CMe_3)]$ (3b**) and $S_{Ir}, S_{C}, S_N-[(\eta^5-C_5Me_5)Ir-(MePro)(C\equiv CMe_3)]$ (**5**).** Single crystals of **3b** separated from **3a/3b** methanolic solution mixtures in higher yield than theoretically expected from the measured composition (¹H NMR) of the solutions. Therefore, an asymmetric transformation of the second kind¹⁶ should be taking place during crystallization. Molecular representations of complexes **3b** and **5** are depicted in Figures 1 and 2, and selected structural parameters are listed in Table 1. In both structures the chiral iridium atom exhibits analogous pseudooctahedral environments. The metal forms its coordination sphere with an η^5 -bonded C₅Me₅ group that occupies three formal coordination sites, the chelating L-proline (**3b**) or N-methyl-L-proline (**5**) ligands, bonded through a carboxylic oxygen and the aminic nitrogen, and a carbon atom of the alkynyl ligand. Although the donor atoms are identical in both complexes, their spatial distribution differs and generates different configurational chirality at the metal atom. In accord with the ligand priority sequence¹⁷ $\eta^5-C_5Me_5 > O > N > C$, the absolute

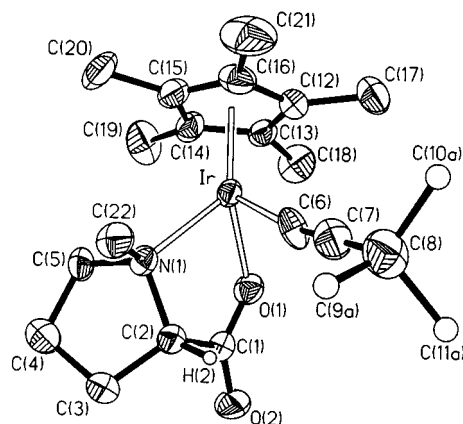


Figure 2. Molecular diagram of the metal complex $S_{Ir}, S_{C}, S_N-[(\eta^5-C_5Me_5)Ir-(MePro)(C\equiv CMe_3)]$ (**5**). Hydrogen atom linked to the chiral C(2) atom has also been represented.

configuration at the iridium center is *R* in **3b** and the opposite one, *S*, in **5**. In addition to the chiral metal, the aminic nitrogen also becomes chiral upon coordination, but, as observed in related cases,^{1c,8,18} it always adopts a configuration identical to that of its neighbor chiral carbon atom, C(2), that is *S* in complexes **3b** and **5**.

Both structures are very similar in terms of bonding parameters—bond distances and angles (see Table 1)—but show some significant differences that deserve a comment. The Ir—G (C₅Me₅ centroid) distances, 1.813(3) (**3b**) and 1.797(6) Å (**5**), are statistically equal, with the Ir—C bond distances ranging between approximately 2.13 and 2.23 Å. Interestingly, the longest Ir—C bond length is found, in both structures, with the carbon atom (C(14)) situated nearly transoid to the alkynyl ligand (C(6)—Ir—C(14) 159.7° in **5**). This fact clearly manifests the higher structural trans influence of the alkynyl compared to those of the amino acidate donor atoms.

Another significant difference concerns the alkynyl coordination. The Ir—C(6) bond distance is shorter in **3b**, 2.012(8) Å, than in **5**, 2.051(5) Å, suggesting a greater interaction between the metal and the alkynyl ligand in the unsubstituted proline derivative **3b**. In accord with this, the C(6)—C(7) triple bond shows a longer separation in **3b** than in **5** (1.20(1) vs 1.160(9) Å), which could be associated with a better electronic π -back-donation from the metal to the unsaturated alkyne bond.

The most noticeable distinction of both complexes affects the conformation of the two rings of the amino acidate ligand: the Ir—O(1)—C(1)—C(2)—N(1) metallacycle and the N(1)—C(2)—C(3)—C(4)—C(5) pyrrolidinic ring. Despite the conformational restraint imposed by the unsaturated bond of the carboxylate group, both rings—in both structures—exhibit similar amplitudes in their puckering: 0.207(5) Å metallacycle, 0.362(11) Å pyrrolidinic ring in **3b**, and 0.393(5) and 0.371(5) Å in **5**. However the puckering differs significantly, showing envelope, twist, or mixed structures ($\varphi = 192(2)^\circ$ and $270.6(14)^\circ$ in **3b**; $\varphi = 392.2(8)^\circ$ and $356.3(9)^\circ$ in **5**).¹⁹

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Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes **3b** and **5**

	3b	5		3b	5
Ir–N(1)	2.135(6)	2.158(4)	N(1)–C(5)	1.53(1)	1.506(6)
Ir–O(1)	2.105(5)	2.087(4)	N(1)–C(22)		1.488(6)
Ir–C(6)	2.012(8)	2.051(5)	O(1)–C(1)	1.255(8)	1.283(6)
Ir–C(12)	2.137(8)	2.146(7)	O(2)–C(1)	1.248(9)	1.227(6)
Ir–C(13)	2.162(8)	2.177(6)	C(1)–C(2)	1.53(1)	1.541(7)
Ir–C(14)	2.230(8)	2.212(7)	C(2)–C(3)	1.52(1)	1.536(7)
Ir–C(15)	2.181(7)	2.180(5)	C(3)–C(4)	1.45(1)	1.548(8)
Ir–C(16)	2.162(8)	2.133(7)	C(4)–C(5)	1.47(1)	1.514(8)
Ir–G ^a	1.813(3)	1.797(6)	C(6)–C(7)	1.20(1)	1.160(9)
N(1)–C(2)	1.50(1)	1.503(6)	C(7)–C(8)	1.49(1)	1.496(9)
N(1)–Ir–O(1)	78.3(2)	77.21(14)	O(1)–C(1)–O(2)	123.3(7)	125.2(5)
N(1)–Ir–C(6)	87.8(3)	86.6(2)	O(1)–C(1)–C(2)	119.8(6)	115.3(4)
N(1)–Ir–G ^a	131.6(2)	134.1(2)	O(2)–C(1)–C(2)	116.9(6)	119.4(5)
O(1)–Ir–C(6)	85.6(3)	87.6(2)	N(1)–C(2)–C(1)	109.3(6)	109.2(4)
O(1)–Ir–G ^a	131.8(2)	128.5(2)	N(1)–C(2)–C(3)	103.5(6)	105.5(4)
C(6)–Ir–G ^a	125.2(3)	126.1(3)	C(1)–C(2)–C(3)	116.2(7)	112.6(5)
Ir–O(1)–C(1)	116.3(4)	118.8(3)	C(2)–C(3)–C(4)	105.4(9)	105.5(4)
Ir–N(1)–C(2)	112.8(5)	107.7(3)	C(3)–C(4)–C(5)	104.2(9)	105.0(5)
Ir–N(1)–C(5)	116.0(5)	113.8(3)	N(1)–C(5)–C(4)	105.7(8)	106.1(5)
Ir–N(1)–C(22)		112.9(3)	Ir–C(6)–C(7)	172.0(8)	170.0(6)
C(2)–N(1)–C(5)	106.2(6)	102.9(4)	C(6)–C(7)–C(8)	179(1)	178.1(8)

^a G represents the centroid of the C₅Me₅ rings.**Table 2.** Crystal Data and Data Collection and Refinement for Complexes **3b** and **5**

	3b	5
chem formula	C ₂₁ H ₃₂ IrNO ₂	C ₂₂ H ₃₄ IrNO ₂
fw	522.71	536.70
cryst size, mm	0.61 × 0.62 × 0.62	0.41 × 0.38 × 0.17
cryst syst	orthorhombic	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (no. 19)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (no. 19)
<i>a</i> , Å	9.5178(10)	9.827(2)
<i>b</i> , Å	12.3851(16)	13.531(3)
<i>c</i> , Å	18.5850(17)	16.426(3)
<i>V</i> , Å ³	2190.8(4)	2184.1(8)
<i>Z</i>	4	4
<i>D</i> _{calcd} , g cm ^{−3}	1.585	1.632
<i>μ</i> , mm ^{−1}	6.107	6.128
no. of measd rflns	4633 (2θ ≤ 52°)	6315 (2θ ≤ 55°)
no. of unique rflns	4278 (<i>R</i> _{int} = 0.0315)	5023 (<i>R</i> _{int} = 0.0276)
min, max trasm fact ^a	0.041, 0.057 ^a	0.055, 0.114
no. data/restraints/params	4031/6/226	5021/3/234
<i>R</i> (<i>F</i>) [<i>F</i> ² ≥ 2σ(<i>F</i> ²)] ^b	0.0345	0.0254
<i>wR</i> (all data)	0.0465 ^c	0.0712 ^d

^a The empirical absorption correction applied gave correction factors 0.842 and 1.245.²⁶ ^b *R*(*F*) = Σ||*F*_o| − |*F*_c||/Σ|*F*_o| for 4031 (**3b**) and 4420 (**5**) observed reflections. ^c *wR*(*F*) = Σ[*w*(*F*_o − *F*_c)²]/Σ[*w*(*F*_o)²]; *w*^{−1} = [σ²(*F*_o)² + 0.000765*F*_o²]. ^d *wR*(*F*²) = [Σ[*w*(*F*_o² − *F*_c²)²]/Σ[*w*(*F*_o²)²]]^{1/2}; *w*^{−1} = [σ²(*F*_o²) + (0.1064*P*)² + 2.999*P*], where *P* = [max(*F*_o², 0) + 2*F*_c²]/3.

NOEDIFF measurements²⁰ strongly suggested that complex **5** retained in solution the *S* configuration shown in the solid state. The most determinant result was that irradiation of the *tert*-butyl singlet proton resonance at 1.18 ppm led to enhancement of the signal of the C(2)-H proton at 4.02 ppm. Analogously, saturation of the phenyl multiplet centered at 7.16 ppm of the ruthenium compound [(η⁶-*p*-MeC₆H₄ⁱPr)Ru(Pro)-(C≡CPh)] (**9**) led to enhancement of the signal of the C(asym)-H proton at 3.83 ppm and of the NH proton at 3.98 ppm, which suggests the same *S* configuration at ruthenium for compound **9**.

Configurational Stability of the Complexes. The circular dichroism (CD) spectrum of the iridium complex **5** (Figure 3a) consisted of two maxima centered at 310

and 370 nm, displaying negative and positive Cotton effects, respectively. Similarly, the CD spectrum of the iridium complex **6** (Figure 3a) showed one negative maximum at 308 nm and a positive one at 365 nm. Accordingly, the *S* configuration, which has been found in the crystal structure of **5**, was assigned to complex **6**.

The CD spectrum of the ruthenium compound **9** (Figure 3b) consisted of two maxima centered at 375 and 445 nm, displaying negative and positive Cotton effects, respectively. Similarly the CD spectra of complexes **7**, **8**, and **10** (Figure 3b) showed one negative maximum at ca. 370 nm and a positive one at ca. 430 nm. Taking together these CD data and the above-discussed NOEDIFF results for complex **9**, we propose for the sole diastereomer observed for compounds **8**–**10** and for the major diastereomer of compound **7** the *S* configuration at the metal.

The metal center is configurationally stable in the iridium compounds **5** and **6** as well as in the ruthenium analogues **8**–**10**, their CD and NMR spectra remaining essentially unchanged during several days. However, the ruthenium compound [(η⁶-*p*-MeC₆H₄ⁱPr)Ru(Ala)-(C≡CPh)] (**7**) slowly epimerizes in chloroform, acetone, or methanol. Thus, for example, in chloroform 70/30 molar ratio *S*_{Ru},*S*_C/*R*_{Ru},*S*_C mixtures changed their diastereomeric composition to 45/55, and in acetone 85/15 *S*_{Ru},*S*_C/*R*_{Ru},*S*_C mixtures epimerize to a 60/40 molar ratio composition, after 3 days in both cases.

Freshly prepared solutions of the iridium compounds **3** and **4** exhibited CD spectra (dotted lines in Figures 3c and 3d, respectively) that clearly indicated a pseudo-enantiomorphous relationship with respect to the optically pure products **5** and **6**, since similar morphologies but opposite signs of the Cotton effects were observed. Additionally, inspection of the ¹H NMR spectra of solutions freshly prepared from crystals of **3b** revealed the presence of **3a/3b** mixtures largely enriched (>95%) in **3b**. Fifteen hours later, the CD spectra of **3** and **4** (full lines in Figures 3c and 3d, respectively) presented the same morphologies and signs as those of **5** and **6**, and the ¹H NMR spectra indicated that the **a** labeled

(20) Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analyses*; VCH: New York, 1989.

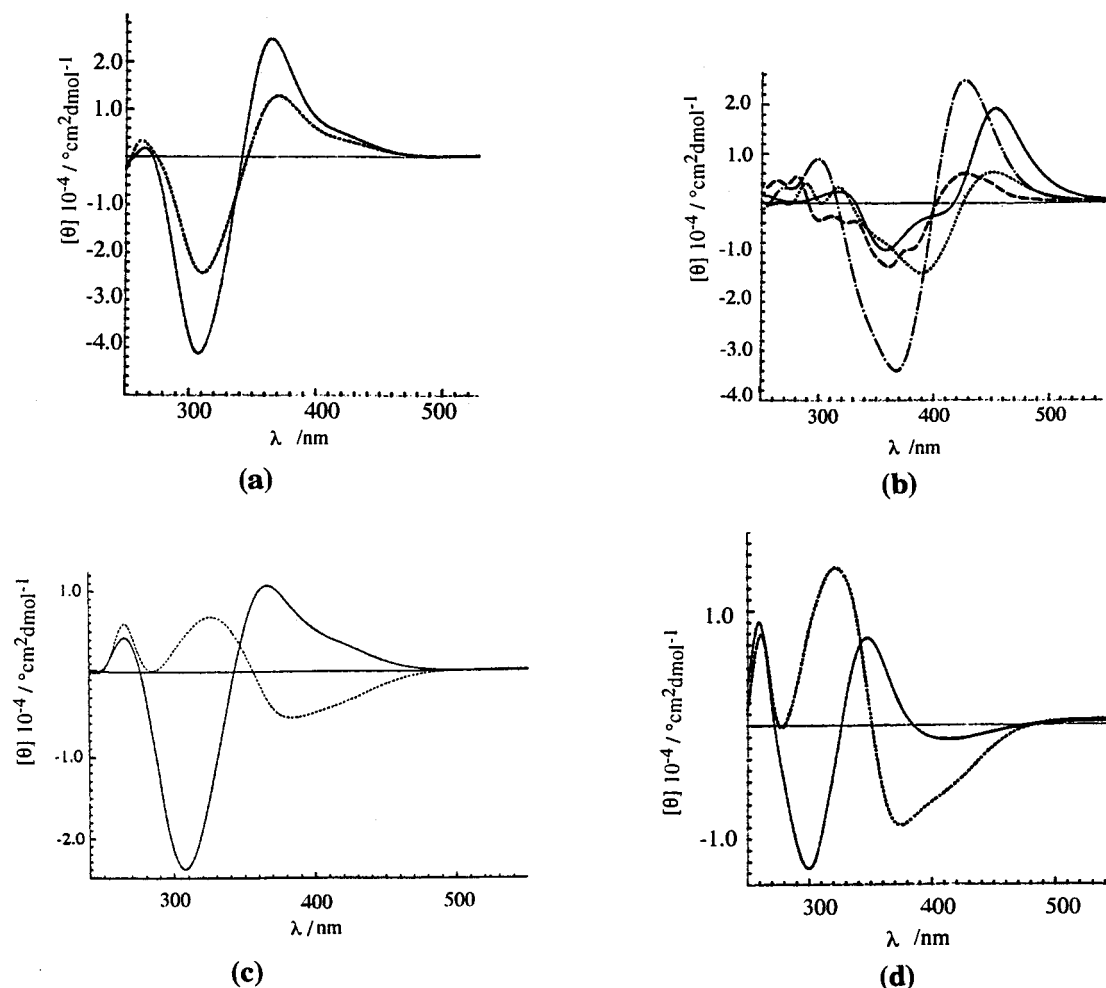


Figure 3. CD spectra (CHCl_3) in the 250–550 nm wavelength range. (a) (···) $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{MePro})(\text{C}\equiv\text{CCMe}_3)]$ (**5**) and (—) $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{MePro})(\text{C}\equiv\text{CSiMe}_3)]$ (**6**). (b) (—) $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}(\text{Pro})(\text{C}\equiv\text{CPh})]$ (**9**), (···) $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}(\text{Ala})(\text{C}\equiv\text{CPh})]$ (**7**), (---) $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}(\text{Ala})(\text{C}\equiv\text{CCO}_2\text{Me})]$ (**8**), and (· · ·) $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}(\text{Pro})(\text{C}\equiv\text{CCO}_2\text{Me})]$ (**10**). (c) $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Pro})(\text{C}\equiv\text{CCMe}_3)]$ (**3**): (···) fresh solutions, (—) 15 hours later. (d) $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Pro})(\text{C}\equiv\text{CSiMe}_3)]$ (**4**): (···) fresh solutions, (—) 15 hours later.

epimers were now the major components. Considering the crystal structure determination of **3b** and the aforementioned results, we concluded that complexes **3** and **4** display the *R* absolute configuration at iridium in the solid state, but when in solution, they slowly epimerized to the isomer that is *S* configured at the metal, which is the thermodynamically preferred epimer for these complexes.¹¹

Epimerization of **3** in chloroform has been monitored by ^1H NMR in the temperature range 293–318 K. Starting from **3b**, the evolution of the **3a** epimer resonances was detected with a concomitant decrease in the intensity of the **3b** epimer resonances. Accurate integration of the NH proton peaks at 5.42 and 4.21 ppm (attributable to the *R* and *S* epimers, respectively) afforded kinetic data. In the range of temperatures measured the epimerization obeyed a first-order rate law (Figure 4a) with derived rate constants ranging from $(2.74 \pm 0.02) \times 10^{-5} \text{ s}^{-1}$ ($t_{1/2} = 6 \text{ h}$, 293 K) to $(61.7 \pm 5.3) \times 10^{-5} \text{ s}^{-1}$ ($t_{1/2} = 0.25 \text{ h}$, 318 K).^{21a} The epimerization was completely displaced to the **3a** isomer, this

product being the sole detectable species in the final solution. From the temperature dependence of the rate constant, the activation parameters $\Delta H^\ddagger = 91.4 \pm 3.4 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -20.8 \pm 10.8 \text{ J K}^{-1} \text{ mol}^{-1}$ were extracted by least-squares^{21b,c} (Figure 4b). Furthermore, an equilibrium constant of 2.70 ± 0.41 has been measured, in methanol at 20 °C, for the process **3b** \rightleftharpoons **3a**, approaching the equilibrium from both sides.

Solutions of the rhodium compounds **1** and **2** showed diastereomeric excesses of only 24% and 8%, respectively, and their CD spectra were not informative. These complexes epimerize in chloroform, but some nonelucidated decomposition processes, which were not further investigated, take place simultaneously.

Epimerization Mechanism. To gain a better insight into the epimerization mechanism, an equimolar mixture of $(R_{\text{Ir}}, S_{\text{C}}, S_{\text{N}})\text{-}[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Pro})(\text{C}\equiv\text{CCMe}_3)]$ (**3b**) and $(S_{\text{Ru}}, S_{\text{C}})/(R_{\text{Ru}}, S_{\text{C}})\text{-}[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}(\text{Ala})(\text{C}\equiv\text{CPh})]$ (**7**) ($S_{\text{Ru}}, S_{\text{C}}/R_{\text{Ru}}, S_{\text{C}}$, 70/30 molar ratio) was allowed to epimerize in methanol at 22 °C. The processes were monitored by ^1H NMR, and this technique clearly showed that both compounds epimerize independently to the corresponding $S_{\text{Ir}}, S_{\text{C}}, S_{\text{N}}$ (**3a**) and $R_{\text{Ru}}, S_{\text{C}}$ derivatives. Thus, no intermolecular processes rendering

(21) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: Weinheim, 1991; (a) p 8; (b) p 87. (c) Morse, P. M.; Spencer, M. O.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

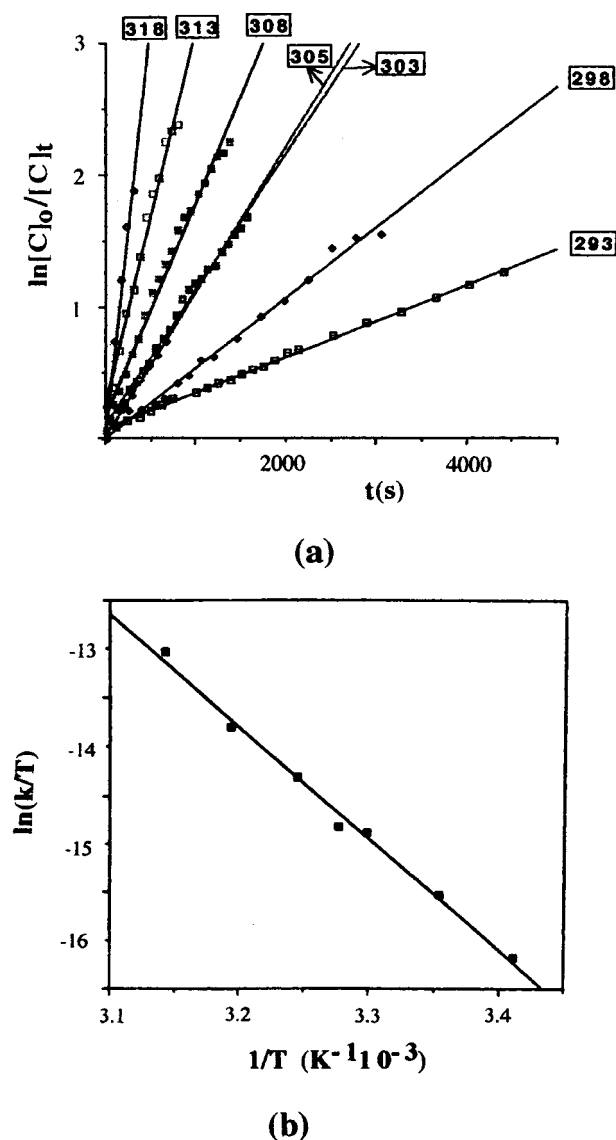


Figure 4. (a) Kinetic and (b) Eyring plots for the epimerization of $(R_{Ir}, S_C, S_N)-[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir(Pro)(C}\equiv\text{CCMe}_3)]$ (**3b**) in CDCl_3 at different temperatures.

compounds containing Ru(Pro) , $\text{Ru(C}\equiv\text{CCMe}_3)$, Ir(Ala) , or $\text{Ir(C}\equiv\text{CPh)}$ moieties have been observed.

Scheme 1 suggests a mechanistic interpretation of the reaction course accounting for all the experimental data observed. The first step of the intramolecular process would imply the cleavage of one of the two ($\text{M}-\text{O}$ or $\text{M}-\text{N}$) metal–amino acidate bonds. Bercaw et al. have established, by NMR spectroscopy, the bond energy sequence $\text{Ru}-\text{C}(\text{sp}) > \text{Ru}-\text{O} > \text{Ru}-\text{N}$ for ruthenium species of formula $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuX}(\text{PMe}_3)_2]$ ($\text{X} = \text{C}\equiv\text{CPh}$, OH , OMe , NHPh , NPh_2).²² On the basis of these results, we tentatively propose the preferential rupture of the $\text{M}-\text{N}$ bond²³ and the formation of the chiral pyramidal species A. In accord with the kinetic data, this would be the rate-determining step. The 16-electron species A would be in equilibrium with its diastereomer C through the planar at-the-metal intermediate B.^{41,n,24}

(22) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.

(23) A mechanism involving the initial rupture of the $\text{M}-\text{O}$ amino acidate bond would be essentially comparable to that described in the text.

Restoration of the $\text{M}-\text{N}$ bond would complete the epimerization. Alternatively, carboxylate complexes D would also be intermediates in the process. The selective cleavage of one of the two $\text{M}-\text{O}$ bonds in D shifts the equilibrium toward the R_M or S_M epimer.

Concluding Remarks

In general, the neutral chloride compounds $[(\eta^n\text{-ring})\text{M}(\text{aa})\text{Cl}]$ react with terminal alkynes $\text{HC}\equiv\text{CR}$ in basic media, rendering the corresponding alkynyl compounds $[(\eta^n\text{-ring})\text{M}(\text{aa})(\text{C}\equiv\text{CR})]$, although, as an exception, the rhodium complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(Ala)Cl}]$ reacts with $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Ph}$, $p\text{-tolyl}$) in the presence of NEt_3 , affording the trisubstituted cyclobutadiene complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\eta^4\text{-C}_4\text{HR}_2\text{C}\equiv\text{CR})]$.^{4t}

The *N*-methylproline alkynyl iridium complexes **5** and **6** and the ruthenium derivatives **8–10** have been isolated with essentially complete diastereoselection and show a remarkable configurational stability in solution. However, the proline rhodium or iridium compounds **1–4** and the alaninate ruthenium complex **7** undergo epimerization processes at metal. In particular, during the crystallization of the iridium compounds **3** and **4** an asymmetric transformation of the second kind occurs: whatever the diastereomeric composition of the solution is, the epimer that is *R* at the metal precipitates in at least 98% spectroscopic purity. These *R*-at-metal epimers slowly epimerize in chloroform, the *S* isomers being the sole detected final products. From kinetic and spectroscopic data, an intramolecular epimerization mechanism has been proposed.

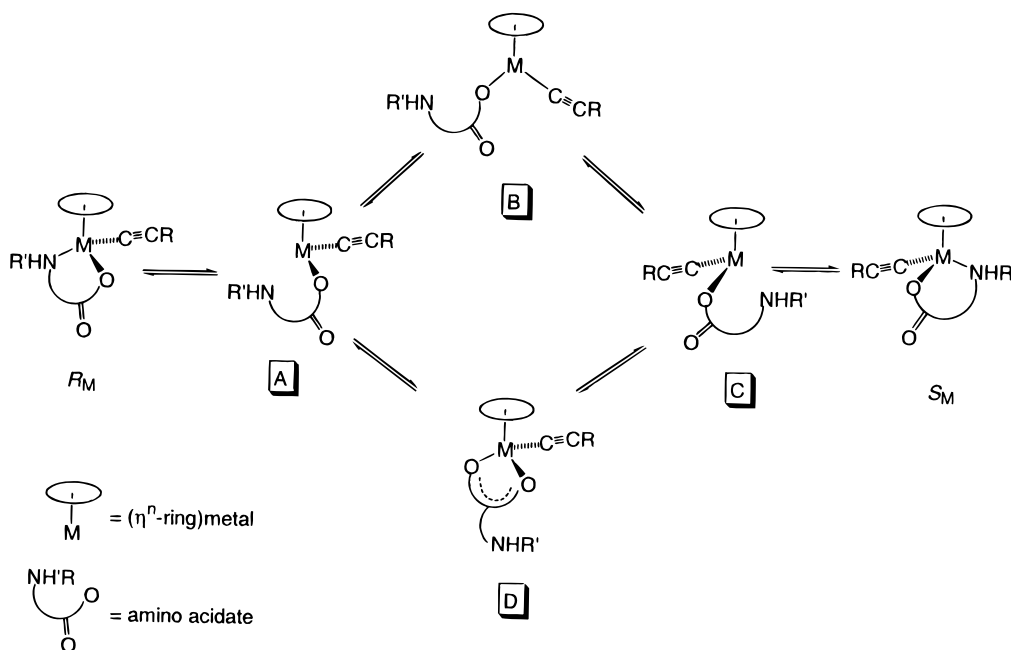
Experimental Section

General Comments. All solvents were dried over appropriate drying agents, distilled under nitrogen, and degassed prior to being used. All preparations have been carried out under a nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed using a Perkin-Elmer 240B microanalyzer. ¹H spectra were recorded on a Varian UNITY 300 (299.95 MHz) or a Bruker 300 ARX (300.10 MHz). Chemical shifts are expressed in ppm upfield from SiMe_4 . CD spectra were determined in CHCl_3 (ca. 10^{-3} mol L^{-1} solutions) in a 1 cm path length cell by using a Jasco-710 apparatus.

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(Pro)(C}\equiv\text{CR)}]$ (1**, **2**).** To a solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(Pro)Cl}]$ (150.0 mg, 0.39 mmol) in methanol (10 mL) were added a methanolic solution of KOH (2.93 mL, 0.1321 mol L^{-1} , 0.39 mmol) and the appropriate alkyne (0.39 mmol). The solution was stirred for 24 h and then vacuum-evaporated to dryness. The residue was extracted with dichloromethane (15 mL) and filtered through kieselguhr. The filtrate was concentrated under reduced pressure to ca. 2 mL. Slow addition of *n*-hexane gave an orange microcrystalline solid, which was filtered off, washed with *n*-hexane, and air-dried. Complex **1**: Yield: 75%; de, 24%. Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{N}_2\text{O}_2\text{Rh}$: C, 58.2; H, 7.4; N, 3.2. Found: C, 58.0; H, 7.2; N, 3.1. IR (Nujol, cm^{-1}): $\nu(\text{NH})$ 3100 (s), $\nu(\text{C}\equiv\text{C})$ 2110 (vs), $\nu(\text{CO})$ 1610 (vs). **1a**: ¹H NMR (CDCl_3): δ 1.17 (s, 9H, CMe_3), 1.66 (s, 15H, C_5Me_5), 1.9–2.3 (m, 4H, CH_2CH_2), 3.18, 3.64 (2xm, 2H, NCH_2),

(24) (a) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536. (b) Bickford, C. C.; Johnson, T. J.; Davidson, E. R.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1080. (c) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488. (d) Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1996**, *15*, 10. (e) Ward, T. R.; Schafer, O.; Daul, C.; Hofmann, P. *Organometallics* **1997**, *16*, 3207. (f) Smith, K. M.; Poli, R.; Legzdins, P. *Chem. Commun.* **1998**, 1903.

Scheme 1. Proposed mechanism for the epimerization of the complexes.



3.72 (m, 1H, CH), 4.40 (m, 1H, NH). **1b**: ^1H NMR (CDCl_3): δ 1.16 (s, 9H, CMe_3), 1.68 (s, 15H, C_5Me_5), 1.9–2.3 (m, 4H, CH_2CH_2), 2.82, 3.40 (2xm, 2H, NCH_2), 4.0 (m, 1H, NH). Complex **2**. Yield: 80%; de, 8%. Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{NO}_2\text{RhSi}$: C, 53.4; H, 7.2; N, 3.1. Found: C, 53.2; H, 6.6; N, 3.1. IR (Nujol, cm^{-1}): $\nu(\text{NH})$ 3140 (s), $\nu(\text{C}\equiv\text{C})$ 2030 (vs), $\nu(\text{CO})$ 1610 (vs). **2a**: ^1H NMR (CDCl_3): δ 0.06 (s, 9H, SiMe_3), 1.69 (s, 15H, C_5Me_5), 1.8–2.4 (m, 4H, CH_2CH_2), 2.80, 3.40 ($2 \times$ m, 2H, NCH_2), 3.82 (m, 1H, CH), 4.00 (m, 1H, NH). **2b**: ^1H NMR (CDCl_3): δ 0.05 (s, 9H, SiMe_3), 1.68 (s, 15H, C_5Me_5), 1.8–2.4 (m, 4H, CH_2CH_2), 3.24, 3.55 ($2 \times$ m, 2H, NCH_2), 3.50 (m, 1H, CH), 5.15 (m, 1H, NH).

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Pro})(\text{C}\equiv\text{CCMe}_3)]$ (3**).** To a solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Pro})\text{Cl}]$ (1000.0 mg, 2.10 mmol) in methanol (50 mL) were added 0.29 mL (2.10 mmol) of NEt_3 and $\text{HC}\equiv\text{CCMe}_3$ (0.27 mL, 2.10 mmol). The solution was stirred for 24 h and then vacuum-evaporated to ca. 2 mL. Slow addition of diethyl ether gave a yellow microcrystalline solid, which was filtered off, washed with 2 mL of water, and air-dried. Yield: 72%; de, 50%. Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{IrNO}_2$: C, 48.3; H, 6.2; N, 2.7. Found: C, 48.2; H, 6.0; N, 2.7. IR (Nujol, cm^{-1}): $\nu(\text{NH})$ 3100 (s), $\nu(\text{C}\equiv\text{C})$ 2110 (vs), $\nu(\text{CO})$ 1625 (vs). **3a**: ^1H NMR (CDCl_3): δ 1.16 (s, 9H, CMe_3), 1.70 (s, 15H, C_5Me_5), 1.80–2.26 (m, 4H, CH_2CH_2), 2.79, 3.41 (2xm, 2H, NCH_2), 4.10 (m, 1H, CH), 4.21 (m, 1H, NH). ^{13}C NMR (CDCl_3): 9.0 (C_5Me_5), 27.0, 28.5 (CH_2CH_2), 29.0 (CMe_3), 33.1 (CMe_3), 54.4 (NCH_2), 63.6 (CH), 80.4 ($\text{C}\equiv\text{CCMe}_3$), 85.9 (C_5Me_5), 110.5 ($\text{C}\equiv\text{CCMe}_3$), 183.0 (CO). **3b**: ^1H NMR (CDCl_3): δ 1.17 (s, 9H, CMe_3), 1.69 (s, 15H, C_5Me_5), 1.94–2.13 (m, 4H, CH_2CH_2), 2.44, 3.22 ($2 \times$ m, 2H, NCH_2), 3.86 (m, 1H, CH), 5.42 (m, 1H, NH).

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Pro})(\text{C}\equiv\text{CSiMe}_3)]$ (4**).** To a solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Pro})\text{Cl}]$ (150.0 mg, 0.31 mmol) in methanol (10 mL) were added 44 μL (0.31 mmol) of NEt_3 and $\text{HC}\equiv\text{CSiMe}_3$ (21 μL , 0.31 mmol). The solution was stirred for 24 h and then vacuum-evaporated to dryness. The residue was dissolved in 2 mL of dichloromethane, and the addition of 5 mL of *n*-hexane produced the precipitation of white Et_3NHCl , which was filtered off. The filtrate was concentrated under reduced pressure, and the yellow microcrystalline solid precipitated was filtered off, washed with *n*-hexane, and air-dried. Yield: 74%; de, 38%. Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{IrNO}_2\text{Si}$: C, 44.6; H, 6.0; N, 2.6. Found: C, 44.3; H, 5.9; N, 2.6. IR (Nujol, cm^{-1}): $\nu(\text{NH})$ 3100 (s), $\nu(\text{C}\equiv\text{C})$ 2030 (vs), $\nu(\text{CO})$ 1620 (vs). **4a**: ^1H NMR (CDCl_3): δ 0.03 (s, 9H, SiMe_3), 1.69 (s, 15H, C_5Me_5), 1.8–2.4

(m, 4H, CH_2CH_2), 2.74, 3.41 ($2 \times$ m, 2H, NCH_2), 4.10 (m, 1H, CH), 4.34 (m, 1H, NH). **4b**: ^1H NMR (CDCl_3): δ 0.02 (s, 9H, SiMe_3), 1.69 (s, 15H, C_5Me_5), 1.8–2.4 (m, 4H, CH_2CH_2), 3.29, 3.72 ($2 \times$ m, 2H, NCH_2), 3.92 (m, 1H, CH), 6.46 (m, 1H, NH).

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{MePro})(\text{C}\equiv\text{CCMe}_3)]$ (5**).** To a solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{MePro})\text{Cl}]$ (300.0 mg, 0.61 mmol) in methanol (15 mL) were added 85 μL (0.61 mmol) of NEt_3 and $\text{HC}\equiv\text{CCMe}_3$ (77 μL , 0.61 mmol). The solution was stirred for 24 h and then vacuum-evaporated to ca. 2 mL. Slow addition of diethyl ether gave a yellow microcrystalline solid, which was filtered off, washed with 2 mL of water, and air-dried. Yield: 40%. Anal. Calcd for $\text{C}_{22}\text{H}_{34}\text{IrNO}_2$: C, 49.2; H, 6.4; N, 2.6. Found: C, 49.0; H, 5.9; N, 2.6. IR (Nujol, cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2115 (vs), $\nu(\text{CO})$ 1635 (vs). ^1H NMR (CDCl_3): δ 1.18 (s, 9H, CMe_3), 1.68 (s, 15H, C_5Me_5), 1.7–2.1 (m, 4H, CH_2CH_2), 2.91 (s, 3H, NMe), 3.22 (m, 2H, NCH_2), 4.02 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1H, CH). ^{13}C NMR (CDCl_3): 9.4 (C_5Me_5), 22.7, 24.6 (CH_2CH_2), 29.0 (CMe_3), 32.9 (CMe_3), 48.9 (NMe), 62.9 (NCH_2), 73.4 (CH), 82.5 ($\text{C}\equiv\text{CCMe}_3$), 85.7 (C_5Me_5), 109.2 ($\text{C}\equiv\text{CCMe}_3$), 182.5 (CO).

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{MePro})(\text{C}\equiv\text{CSiMe}_3)]$ (6**).** To a solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{MePro})\text{Cl}]$ (100.0 mg, 0.20 mmol) in methanol (10 mL) were added 29 μL (0.20 mmol) of NEt_3 and $\text{HC}\equiv\text{CSiMe}_3$ (30 μL , 0.20 mmol). The solution was stirred for 24 h and then vacuum-evaporated to dryness. The residue was extracted with tetrahydrofuran (10 mL) and filtered through kieselguhr. The filtrate was concentrated under reduced pressure to ca. 2 mL. Slow addition of *n*-hexane gave a yellow microcrystalline solid, which was filtered off, washed with *n*-hexane, and air-dried. Yield: 70%. Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{IrNO}_2\text{Si}$: C, 45.6; H, 6.2; N, 2.5. Found: C, 45.2; H, 5.8; N, 2.5. IR (Nujol, cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2040 (vs), $\nu(\text{CO})$ 1650 (vs). ^1H NMR (CDCl_3): δ 0.04 (s, 9H, SiMe_3), 1.66 (s, 15H, C_5Me_5), 1.7–2.1, 2.4 ($2 \times$ m, 4H, CH_2CH_2), 2.92 (s, 3H, NMe), 3.20 (m, 2H, NCH_2), 4.00 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H, CH).

Preparation of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}(\text{aa})(\text{C}\equiv\text{CR})]$ (7–10**).** To a solution of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})\text{Ru}(\text{aa})\text{Cl}]$ (aa = Ala, Pro) (0.39 mmol) in methanol (10 mL) were added a methanolic solution of KOH (1.36 mL, 0.2864 mol L^{-1} , 0.39 mmol) and the appropriate alkyne (0.39 mmol). The solution was stirred for 5 h and then vacuum-evaporated to dryness. The residue was extracted with dichloromethane (15 mL) and filtered through kieselguhr. The filtrate was concentrated under reduced pressure to ca. 2 mL. Slow addition of diethyl ether gave an orange microcrystalline solid, which was filtered off,

washed with diethyl ether, and air-dried. Complex **7**. Yield: 85%; de, 40%. Anal. Calcd for $C_{21}H_{25}NO_2Ru$: C, 59.4; H, 5.9; N, 3.3. Found: C, 59.6; H, 6.0; N, 3.2. IR (Nujol, cm^{-1}): $\nu(NH)$ 3100 (s), $\nu(C\equiv C)$ 2102 (vs), $\nu(CO)$ 1610 (vs). **7a**: 1H NMR ($CDCl_3$): δ 1.16–1.25 (m, p -MeC₆H₄Me₂CH, overlapped with the corresponding **7b** resonances), 1.39 (d, $^3J_{HH} = 7.3$ Hz, 3H, Ala Me), 2.13 (s, 3H, p -MeC₆H₄iPr), 2.76 (sp, 1H, p -MeC₆H₄-Me₂CH), 3.44 (m, 1H, C_{asym}H), 5.13–5.62 (m, p -MeC₆H₄iPr, overlapped with the corresponding **7b** resonances), 5.30 (m, 1H, NH), 7.02–7.24 (m, Ph, overlapped with the corresponding **7b** resonances). **7b**: 1H NMR ($CDCl_3$): δ 2.11 (s, 3H, p -MeC₆-H₄iPr), 2.60 (m, 1H, C_{asym}H). Complex **8**: Yield: 88%. Anal. Calcd for $C_{17}H_{23}NO_2Ru$: C, 51.8; H, 5.9; N, 3.5. Found: C, 52.0; H, 5.8; N, 3.4. IR (Nujol, cm^{-1}): $\nu(NH)$ 3100 (s), $\nu(C\equiv C)$ 2097 (vs), $\nu(CO)$ 1620 (vs). 1H NMR ($CDCl_3$): δ 1.20, 1.22 ($2 \times$ d, $^3J_{HH} = 6.6$ Hz, 6H, p -MeC₆H₄Me₂CH), 2.13 (s, 3H, p -MeC₆H₄iPr), 2.20 (d, $^3J_{HH} = 7.2$ Hz, 3H, Ala Me), 2.73 (sp, 1H, p -MeC₆H₄-Me₂CH), 3.63 (s, 3H, CO₂Me), 3.72 (m, 1H, C_{asym}H), 3.90 (m, 1H, NH), 5.00 (m, 1H, NH), 5.13, 5.31 (AB system, $J_{AB} = 5.8$ Hz, p -MeC₆H₄iPr), 5.48, 5.58 (AB system, $J_{AB} = 6.0$ Hz, p -MeC₆H₄iPr). Complex **9**: Yield: 80%. Anal. Calcd for $C_{23}H_{27}NO_2Ru$: C, 61.3; H, 6.0; N, 3.1. Found: C, 61.1; H, 5.8; N, 3.1. IR (Nujol, cm^{-1}): $\nu(NH)$ 3098 (s), $\nu(C\equiv C)$ 2104 (vs), $\nu(CO)$ 1634 (vs). 1H NMR ($CDCl_3$): δ 1.24, 1.26 ($2 \times$ d, $^3J_{HH} = 6.6$ Hz, 6H, p -MeC₆H₄Me₂CH), 1.93–2.09 ($2 \times$ m, 4H, CH₂CH₂), 2.10 (s, 3H, p -MeC₆H₄iPr), 2.81 (sp, 1H, p -MeC₆H₄Me₂CH), 2.83, 3.65 ($2 \times$ m, 2H, NCH₂), 3.83 (m, 1H, C_{asym}H), 3.98 (m, 1H, NH), 5.07, 5.20 (AB system, $J_{AB} = 5.7$ Hz, p -MeC₆H₄iPr), 5.55, 5.73 (AB system, $J_{AB} = 5.6$ Hz, p -MeC₆H₄iPr), 7.16 (m, 5H, Ph). Complex **10**: Yield: 82%. Anal. Calcd for $C_{19}H_{25}NO_2Ru$: C, 52.8; H, 5.8; N, 3.2. Found: C, 52.6; H, 5.7; N, 3.1. IR (Nujol, cm^{-1}): $\nu(NH)$ 3098 (s), $\nu(C\equiv C)$ 2100 (vs), $\nu(CO)$ 1620 (vs). 1H NMR ($CDCl_3$): δ 1.23, 1.25 ($2 \times$ d, $^3J_{HH} = 6.7$ Hz, 6H, p -MeC₆H₄Me₂CH), 1.69–2.12 (m, 4H, CH₂CH₂), 2.10 (s, 3H, p -MeC₆H₄iPr), 2.76 (sp, 1H, p -MeC₆H₄Me₂CH), 2.96, 3.67 ($2 \times$ m, 2H, NCH₂), 3.64 (s, 3H, CO₂Me), 3.79 (m, 1H, C_{asym}H), 3.99 (m, 1H, NH), 5.19, 5.31 (AB system, $J_{AB} = 6.0$ Hz, p -MeC₆H₄iPr), 5.48, 5.58 (AB system, $J_{AB} = 5.8$ Hz, p -MeC₆H₄iPr). ^{13}C NMR ($CDCl_3$): 18.6 (p -MeC₆H₄iPr), 22.4, 22.7 (p -MeC₆H₄Me₂CH), 27.0, 28.4 (CH₂CH₂), 31.0 (p -MeC₆H₄Me₂CH), 51.8 (CO₂Me), 58.1 (CH₂NH), 63.1 (C_{asym}), 81.2, 81.4, 87.7, 88.3, 99.5, 101.3 (p -MeC₆H₄iPr), 105.6 (C=CCO₂Me), 123.1 (C=CCO₂Me), 153.9 (CO₂Me), 181.7 (CO).

Epimerization of R_{Ir}, S_C, S_N -[(η^5 -C₅Me₅)Ir(Pro)(C \equiv CC-Me₃)] (3b**) in $CDCl_3$.** The rates were measured by 1H NMR. Probe temperatures were calibrated with methanol. Prior to rate data acquisition, samples were allowed to equilibrate for 5 min. Under a nitrogen atmosphere, a 5 mm NMR tube was charged with 8.0 mg (0.015 mmol) of R_{Ir}, S_C, S_N -[(η^5 -C₅Me₅)Ir(Pro)(C \equiv CCMe₃)] (**3b**) and 0.6 mL of $CDCl_3$. The resulting suspension was vigorously agitated until the solid was completely dissolved. Then, the tube was transferred to the probe, which was maintained at the corresponding constant temperature: 293, 298, 303, 305, 308, 313, or 318 K. The 1H NMR spectra were recorded at measured time intervals. The diastereomeric composition was determined from the integrals of the aminic protons at 5.42 (R_{Ir}, S_C, S_N -**3** (**3b**)) and at 4.21 ppm (S_{Ir}, S_C, S_N -**3** (**3a**)). In all seven experiments only the S -at-metal **3a** epimer was detected at the end of the epimerization. The data could be fit by a least-squares analysis to $\ln(C_0/C_t) = Kt$ where C_0 is the initial mole fraction of the R -at-metal isomer and C_t is the mole fraction at time t . The first-order rate constant, K , extracted from the slope of the least-squares-determined curve was ($\times 10^{-5}, s^{-1}$) 2.74 \pm 0.02, 5.36 \pm 0.13, 10.38 \pm 0.18, 11.06 \pm 0.19, 18.78 \pm 0.32, 28.73 \pm 1.36, and 61.7 \pm 5.3 at 293, 298, 303, 305, 308, 313, and 318 K, respectively.

Equilibration of R_{Ir}, S_C, S_N - and S_{Ir}, S_C, S_N -[(η^5 -C₅Me₅)Ir(Pro)(C \equiv CCMe₃)] (3**) in CD_3OD .** A 5 mm NMR tube was charged with 8.0 mg (0.015 mmol) of R_{Ir}, S_C, S_N -**3** (**3b**) and 0.6 mL of CD_3OD . 1H NMR spectra were recorded at 20 °C at

measured time intervals. After 6 h the diastereomeric composition was **3a/3b** = 2.70 \pm 0.41. Similarly, a solution of S_{Ir}, S_C, S_N -**3** (**3a**) (8.0 mg, 0.015 mmol) in 0.6 mL of CD_3OD was checked periodically by 1H NMR. After 13 h the diastereomeric composition was **3a/3b** = 2.70 \pm 0.41.

Determination of Crystal Structures of R_{Ir}, S_C, S_N -[(η^5 -C₅Me₅)Ir(Pro)(C \equiv CCMe₃)] (3b**) and S_{Ir}, S_C, S_N -[(η^5 -C₅Me₅)Ir(MePro)(C \equiv CCMe₃)] (**5**).** Single crystals for the X-ray diffraction studies were obtained by slow diffusion of diethyl ether into concentrated solutions of the complexes in methanol. A summary of crystal data and intensity collection and refinement parameters is reported in Table 2. The orange (**3b**) or yellow (**5**) crystals used for the X-ray analyses were glued to a glass fiber, mounted on a Siemens-Stoe AED-2 diffractometer, and irradiated with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Cell constants were obtained from the least-squares fit on the setting angles of 50 reflections ($20^\circ \leq 2\theta \leq 40^\circ$) (**3b**) or 48 reflections ($20^\circ \leq 2\theta \leq 32^\circ$). A complete set of independent reflections with 2θ up to 52° ($-12 \leq h \leq 12$, $-15 \leq k \leq 0$, and $0 \leq l \leq 23$) for **3b**, or 55° ($-12 \leq h \leq 0$, $0 \leq k \leq 17$, and $-21 \leq l \leq 21$) for **5**, was measured at 295(2) K for each crystal, using the $\omega/2\theta$ scan technique. Three standard reflections were monitored every 55 min of measuring time throughout data collection as a check on crystal and instrument stability; no decay was observed. Both data were corrected for Lorentz and polarization effects. Reflections were also corrected for absorption using a semiempirical (Ψ -scan)²⁵ or an empirical method (ΔF).²⁶

Both structures were solved by Patterson and subsequent difference Fourier techniques and refined by full-matrix least-squares on F (SHELX-76)²⁷ or F^2 (SHELXL-97).²⁸ In both structures the three terminal methyl groups of the *tert*-butylethynyl ligand were observed disordered (C(9), C(10), and C(11) atoms). Two positions were refined for each carbon atom with isotropic displacement parameters and complementary occupancy factors. Anisotropic displacement parameters were included for all nondisordered non-hydrogen atoms. All hydrogen atoms, except those of the disordered methyl groups, were included in the last cycles of refinement, most of them from calculated positions. All were refined riding on their carbon atoms with a common thermal parameter. Although a chiral internal reference was present in both complexes (C(2) atom), the absolute structure was checked by Rogers ($\eta = 1.03(3)$, **3b**) or Flack ($x = -0.010(12)$, **5**) methods.²⁹ The function minimized for **3b** was $\sum[w(F_o - F_c)^2]$ with a weighting system $w^{-1} = [\sigma^2(F_o^2) + 0.000765F_o^2]$. For **5** the function minimized was $\sum[w(F_o^2 - F_c^2)^2]$. The calculated weighting scheme was $1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$; all the refinements converged to reasonable R factors (see Table 2). The highest residual electron density peaks in both structures were situated in close proximity to the metal atoms and have no chemical sense. Scattering factors were used as implemented in the refinement program.²⁷

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Supporting Information Available: An X-ray crystallographic file for complexes **3b** and **5** is available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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