Stereochemistry at carbon upon protonolysis of a late transition metal-alkyl bond: a reaction of relevance to catalytic enantioselective hydrogenation of olefins

Jason A. Wiles, Steven H. Bergens, and Victor G. Young, Jr.

Abstract: Reaction of [Ru((*R*)-BINAP)(H)(MeCN)$_n$(acetone)$_{3-n}$](BF$_4$) (where n = 0–3) (**2**) with 1 equiv of the olefin substrate methyl α-acetamidoacrylate (MAA) in acetone at room temperature immediately generated a mixture (72:28) of two diastereomers of the complex [Ru((*R*)-BINAP)(MeCN)(MAA(H))](BF$_4$) (**3**). The olefin–hydride insertion reaction between **2** and MAA to generate **3** was regioselective, with transfer of the hydride to the β-olefinic carbon and transfer of ruthenium to the α-carbon in both diastereomers of **3**. The two diastereomers of **3** differ by the absolute configuration at the α-carbon of MAA(H) (($S_{C\alpha}$)-**3** and ($R_{C\alpha}$)-**3**). The absolute configuration of the major (($S_{C\alpha}$)-**3**) diastereomer was determined by X-ray diffraction in conjunction with NMR spectroscopic data. Protonolysis of the ruthenium–carbon bond in **3** and in the methyl α-acetamidocinnamate (MAC) analog ([Ru((*R*)-BINAP)(MeCN)((*S*)-MAC(H))](BF$_4$) (($S_{C\alpha}$)-**4**)) by addition of 2 equiv HBF$_4$·Et$_2$O in CH$_2$Cl$_2$ at room temperature was not stereospecific and did not occur with β-hydride elimination from the methyl or benzyl groups.

Key words: ruthenium, BINAP, enantioselective, hydrogenation, catalysis.

Résumé : La réaction du [Ru((*R*)-BINAP(H)(MeCN)$_n$(acétone)$_{3-n}$](BF$_4$) (dans lequel n = 0–3) (**2**) avec un équivalent du substrat oléfinique α-acétamidoacétate de méthyle ("MAA"), dans l'acétone, à la température ambiante, conduit immédiatement à la formation d'un mélange (72:28) de deux diastéréomères du complexe [Ru((*R*)-BINAP(MeCN)("MAA"(H))](BF$_4$) (**3**). La réaction d'insertion oléfine–hydrure entre **2** et "MAA" pour générer **3** est régiosélective; dans les deux diastéréomères de **3**, le transfert de l'hydrure se portant sur le carbone oléfinique β et le transfert de ruthénium sur le carbone α. Les deux diastéréomères de **3** diffèrent par la configuration absolue au niveau du carbone en α du "MAA"(H) (($S_{C\alpha}$)-**3**) et (($R_{C\alpha}$)-**3**). On a déterminé la configuration absolue du produit principal, le diastéréomère (($S_{C\alpha}$)-**3**), par diffraction des rayons X alliée aux données de spectroscopie RMN. La protonolyse de la liaison ruthénium–carbone présente dans le composé **3** et dans son analogue α-acétamidocinnamate de méthyle ("MAC"), le [Ru((*R*)-BINAP(MeCN)((*S*)-"MAC"(H))](BF$_4$) (($S_{C\alpha}$)-**4**), a été réalisée par addition de deux équivalents de HBF$_4$·Et$_2$O, dans du CH$_2$Cl$_2$, à la température ambiante; cette réaction n'est pas stéréospécifique et elle ne se produit pas par le biais d'une élimination β à partir des groupes méthyle ou benzyle.

Mots clés : ruthénium, BINAP, énantiosélective, hydrogénation, catalyseur.

[Traduit par la Rédaction]

Introduction

The first reported use of ruthenium complexes as homogeneous catalysts for hydrogenation of olefins was a landmark paper published by James and co-workers (1) nearly 40 years ago. This paper, in part, laid the groundwork for James' further development of the first enantioselective catalytic hydrogenation using a ruthenium catalyst containing a chiral bis(phosphine) ligand (2). These papers helped found and inspire the development of ruthenium – chiral bis(phosphine) catalysts, the most versatile and widely used catalyst systems for the enantioselective hydrogenation of olefins and ketones.

The mechanisms for hydrogenations catalyzed by ruthenium–bis(phosphine)-halide complexes, as well as the chemistry of such compounds, have been extensively studied by James et al. (3). Mechanistic studies by James, Noyori, and others showed that hydrogenation of α,β-unsaturated acids (e.g., tiglic acid ((*E*)-CH$_3$CH=C(CH$_3$)CO$_2$H)) using Ru((*R*)-BINAP)(O$_2$CCH$_3$)$_2$ (**1**) as catalyst in MeOH proceeds by heterolytic cleavage of H$_2$ and subsequent protonolysis of a ruthenium(II)–alkyl bond (4). As the putative ruthenium(II)–alkyl intermediate occurred after the turnover-limiting step in the catalytic cycle, it was impossible to detect in solution, and the stereochemistry of this key enantio-determining step

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Dedicated to Professor Brian James on the occasion of his 65th birthday.

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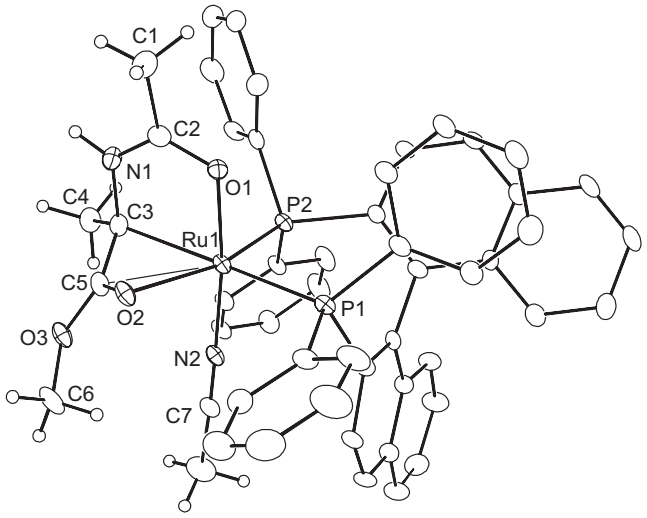
could not be directly observed. A comparison of NMR data for the isotopomers of $CH_3CHDCD(CH_3)CO_2H$ obtained from deuterations of tiglic acid in MeOD using **1** and using $RhCl(PPh_3)_3$ as a catalyst lead to the conclusion that protonolysis proceeded via retention of configuration at carbon (*4b*). Most catalytic hydrogenations of olefins that involve protonolysis (solvolysis) of a metal–carbon bond are believed to, or have been shown to, proceed via a net *syn*-addition of H_2 across the olefin; the presumed consequence of retention at carbon during the protonolysis. There are reported examples, however, for which direct protonolysis of Pt–C σ bonds through back-side attack was postulated to account for catalytic net *anti*-addition of deuterium to certain olefins using platinum–tin complexes as catalysts (5). We now report the first direct observations of protonolysis of the catalyst–alkyl bond in two putative diastereomeric intermediates for catalytic hydrogenation of olefins.

Results and discussion

Reaction of [Ru((*R*)-BINAP)(H)$(MeCN)_n(acetone)_{3-n}$](BF_4) (where n = 0–3) (**2**) (6) with 1 equiv of methyl α-acetamidoacrylate (MAA) in acetone at room temperature generated upon mixing (>99% by NMR analysis) a mixture of two species in a ratio of 72:28 (eq. [1]).

NMR spectroscopy, electrospray-ionization mass spectrometry (EI-MS), and microanalysis indicated that these species were two diastereomeric forms of the complex [Ru((*R*)-BINAP)(MeCN)(MAA(H))](BF_4) (**3**). Complex **3** resulted from olefin–hydride insertion between MAA and **2**. We previously reported the preparation, solid-state structure, and reactivity of a related complex formed by reaction between **2** and methyl α-acetamidocinnamate (MAC) in >99% diastereomeric excess (de), viz., [Ru((*R*)-BINAP)(MeCN)((*S*)-MAC(H))](BF_4) ($(S_{C\alpha})$-**4**) (6). In accord with $(S_{C\alpha})$-**4**, the olefin–hydride insertion reaction between **2** and MAA was regioselective, with transfer of the hydride to the β-olefinic carbon in MAA and transfer of ruthenium to the α-carbon in both diastereomers of **3** (for similar regioselective insertion of MAA into Ru–H bonds of chiral clusters, see ref. 7). NMR chemical shifts and coupling constants for both diastereomers of **3** parallel those previously found for $(S_{C\alpha})$-**4**. For example, $^{13}C\{^1H\}$ NMR signals from the coordinated amido and the ester carbonyls, as well as from the α-carbon of **3** (that σ-bonded to ruthenium) are comparable to those of $(S_{C\alpha})$-**4**. From these similarities, we conclude that the two diastereomers of **3** differ by the absolute configuration at the α-carbon of MAA(H) ($(S_{C\alpha})$-**3** and $(R_{C\alpha})$-**3**). The absolute configuration of the major (72%) diastereomer was determined as follows.

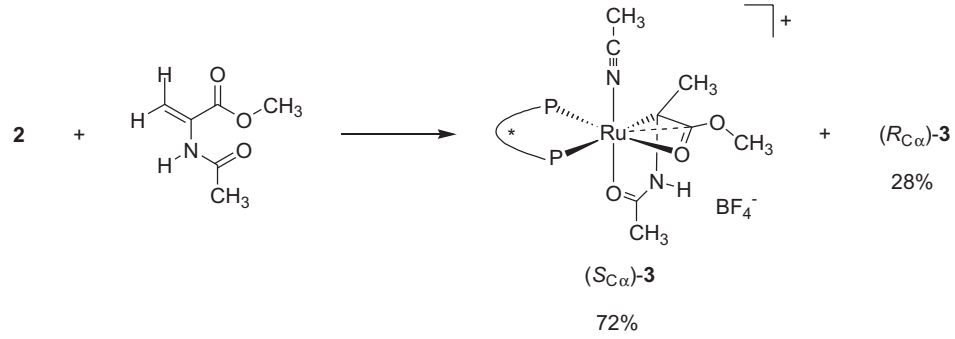
Fig. 1. Structure of $(S_{C\alpha})$-**3** as determined by X-ray diffraction.[2,3]



Slow liquid–liquid diffusion of di-*n*-butyl ether into a 1,2-dimethoxyethane solution of **3** (72:28) at room temperature produced X-ray quality crystals.[2] Diffraction data was collected from two separate samples. In both cases, the molecular structure of the isolated species was of $(S_{C\alpha})$-**3**, as shown in Fig. 1. The molecular structures of $(S_{C\alpha})$-**3** and $(S_{C\alpha})$-**4** are quite similar.

Both are best described as the enolates of $MAA(H)^-$ and $MAC(H)^-$ bonded to ruthenium through Cα (C3) and through

[1]



[2] Crystal data for $(S_{C\alpha})$-**3**: $C_{52}H_{45}BF_4N_2O_3P_2Ru$, FW = 995.72, yellow plate, crystal size 0.40 × 0.25 × 0.13 mm, orthorhombic, $C222_1$, a = 21.4849(2), b = 29.7175(2), c = 18.8513(2) Å, V = 12036.1(2) Å^3, Z = 8, $\rho_{calcd.}$ = 1.099 g cm^{-3}, μ (Mo Kα) = 0.361 mm^{-1}, T = 173(2) K, λ (Mo Kα) = 0.71073 Å. Data were collected using a Siemens SMART Platform CCD diffractometer (θ range for data collection of 1.17 to 25.04°); 10589 independent reflections (8758 with $F_o^2 > 2\sigma(F_o^2)$) were measured. The structure was solved via direct methods (SHELXTL-V5.0). Full-matrix least-squares refinement on F^2 (SHELXTL-V5.0) yielded R_1 = 0.0480 ($F_o^2 > 2\sigma(F_o^2)$) and wR_2 = 0.1261 (all data). GoF on F^2 = 1.041.

the amido and ester carbonyl groups.[3] To determine if ($S_{C\alpha}$)-**3** was the major or minor diastereomer, the crystal used for one of the two structure determinations was dissolved at –78°C in CD_2Cl_2. The ^1H NMR spectrum revealed a 95:5 (major:minor) mixture of the diastereomers of **3** within the crystal.[4] These X-ray and NMR data show that the major diastereomer of **3** formed by reaction of MAA and **2** is ($S_{C\alpha}$)-**3**. As stated above, use of MAC results in almost exclusive formation of this diastereomer (($S_{C\alpha}$)-**4**).[5]

Crystals of the minor diastereomer suitable for X-ray diffraction could not be obtained. In an attempt to confirm that it was ($R_{C\alpha}$)-**3**, we effected the protolytic cleavage of the Ru–Cα bond with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 solution. Addition of 2 equiv $HBF_4{\cdot}Et_2O$ to a solution of **3** (72:28) in CH_2Cl_2 at room temperature followed by addition of excess MeCN (9.5 equiv) generates *N*-acetylalanine methyl ester ($MAA(H)_2$) and the known dicationic compound [Ru((*R*)-BINAP)$(MeCN)_4$]$(BF_4)_2$ (8). Protonolysis with retention of configuration at Cα of the mixture of ($S_{C\alpha}$)-**3** and ($R_{C\alpha}$)-**3** (72:28) will generate $MAA(H)_2$ in 44% (*R*) enantiomeric excess (ee) (72% (*R*)-$MAA(H)_2$ and 28% (*S*)-$MAA(H)_2$). The ee of the $MAA(H)_2$ isolated from the protonolysis was 44% (*S*); the protonolysis of the Ru–C bond in **3** occurred with apparent inversion of configuration at carbon.[6] This experiment was repeated twice.

Two control experiments showed that ($S_{C\alpha}$)-**3** and ($R_{C\alpha}$)-**3** do not interconvert in the absence of acid under these conditions. First, the compositions of 72:28 and 95:5 mixtures of these diastereomers did not change over several days in CH_2Cl_2 at room temperature. Second, exposure of **3** to D_2 (1 atm, 1 atm = 101.325 kPa) at room temperature does not result in H–D exchange at Cβ (Ru-Cα-C*H*$_3$). We previously showed that formation of the MAC analogue (($S_{C\alpha}$)-**4**) is reversible under these conditions using a similar experiment (6*b*). Specifically, exposure of ($S_{C\alpha}$)-**4** to D_2 (1 atm) resulted in H–D exchange at Cβ of MAC(H) (Ru-Cα-C*H*$_2$Ph) via β-hydride elimination and subsequent H–D exchange at the ruthenium-hydride. Thus, conversion between ($S_{C\alpha}$)-**3** and ($R_{C\alpha}$)-**3** did not occur to an appreciable extent prior to reaction with acid.

There is the possibility that reaction of **3** with $HBF_4{\cdot}Et_2O$ generated dicationic diastereomeric ruthenium(IV)–hydrido-alkyl complexes ($S_{C\alpha}$)-**3′** and ($R_{C\alpha}$)-**3′** by protonation at the ruthenium centre. These dicationic diastereomers could in principle interconvert via β-H elimination from the methyl group before elimination of $MAA(H)_2$. To investigate this possibility, we prepared **3**-d_1 (in which one β-H of Ru-Cα-C*H*$_3$ was replaced by deuterium, prepared by reaction of **2**-d_1 with MAA) and reacted it with 2 equiv $HBF_4{\cdot}Et_2O$. After treatment with MeCN and purification, the recovered $MAA(H)_2$ consisted of $MAA(H)_2$-β-d_1 as the sole isotopomer. β-H elimination at the methyl group of **3′**, face flip of the coordinated olefin, and olefin–hydride insertion is expected to cause some scrambling of deuterium between the α- and β-positions of $MAA(H)_2$. The absence of any such scrambling shows that if the dicationic diastereomers ($S_{C\alpha}$)-**3′** and ($R_{C\alpha}$)-**3′** do form, they do not interconvert via β-H elimination from the methyl group.

Although these experiments indicated that protonolysis of the ruthenium–carbon bonds in ($S_{C\alpha}$)-**3** and ($R_{C\alpha}$)-**3** proceeded by inversion, protonation of a sample enriched in ($S_{C\alpha}$)-**3** (95:5) using 2 equiv $HBF_4{\cdot}Et_2O$ yielded, after treatment with MeCN and purification, $MAA(H)_2$ in 44% ee (*S*). This is the same ee as that obtained from the 72:28 mixture of ($S_{C\alpha}$)-**3** and ($R_{C\alpha}$)-**3**, respectively, and it shows that the protonolysis is not stereospecific. This result is confirmed by protonolysis of ($S_{C\alpha}$)-**4**-d_1, the MAC derivative of ($S_{C\alpha}$)-**3**-d_1 (where one β-H of Ru-Cα-C*H*$_2$Ph was replaced by deuterium), prepared by reaction of **2**-d_1 with MAC (6*a*). Reaction of ($S_{C\alpha}$)-**4**-d_1 with 2 equiv $HBF_4{\cdot}Et_2O$ yielded, after treatment with MeCN and purification, $MAC(H)_2$-β-d_1 as the sole isotopomer in 12% ee (*R*). Thus, protonolysis of the ruthenium–carbon bond in ($S_{C\alpha}$)-**4**-d_1 is also not stereospecific, and it too does not involve β-H elimination from the benzyl group.

Conclusions

Our previous report of the MAC compound ($S_{C\alpha}$)-**4** was the first solid-state structure of a diastereomeric catalyst–substrate complex of the same absolute configuration as the major product enantiomer of an olefin hydrogenation. This report of the MAA compound ($S_{C\alpha}$)-**3** is the second; as such, it adds to the sparse knowledge base of the structures of these diastereomeric putative catalytic intermediates. Reaction of MAC with **2** favours almost exclusive formation of

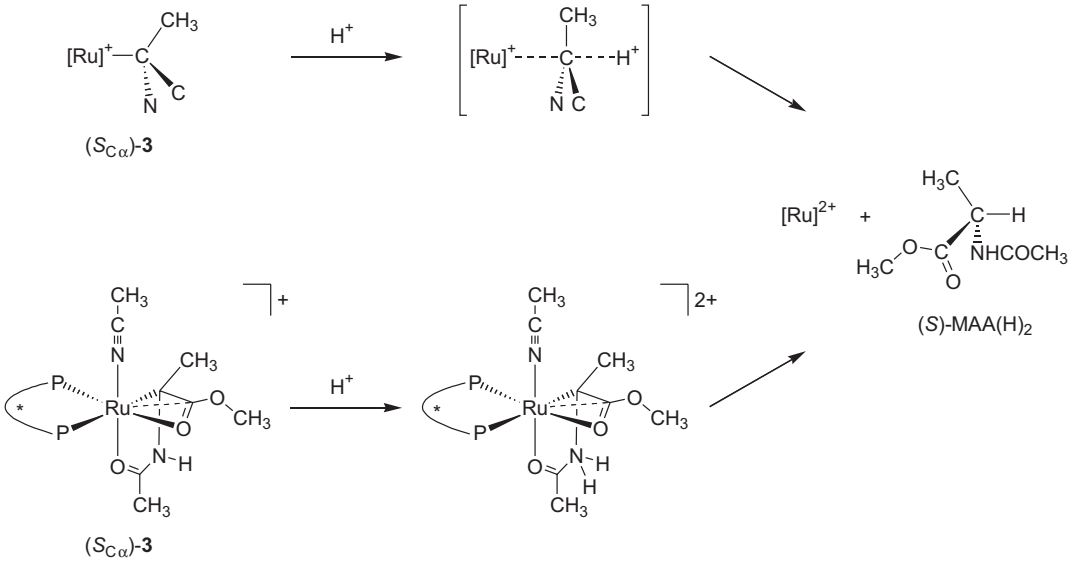
[3] Selected bond lengths (Å) and angles (°) with estimated standard deviations for ($S_{C\alpha}$)-**3** are as follows: Ru(1)—N(2) 1.995(4), Ru(1)—P(1) 2.3525(13), Ru(1)—P(2) 2.2640(11), Ru(1)—O(1) 2.072(3), Ru(1)—O(2) 2.278(3), Ru(1)—C(3) 2.230(5), Ru(1)—C(5) 2.345(5), C(3)—C(4) 1.515(7) Å; C(5)-C(3)-C(4) 119.1(4), N(1)-C(3)-C(5) 112.1(4), N(1)-C(3)-C(4) 111.4(4), Ru(1)-C(3)-N(1) 101.4(4), Ru(1)-C(3)-C(4) 132.0(3), Ru(1)-C(3)-C(5) 76.1(3)°.

[4] We both dissolved the crystal and analyzed the resulting solution at low temperature to prevent any diastereomeric interconversion that may occur. This precaution was not necessary as ^{31}P NMR spectroscopic analysis of **3** (72:28 and 95:5 (major:minor) diastereomeric ratios) in acetone-d_6 over a range of temperatures from –80 to +25°C showed the ratios of diastereomers did not vary under these conditions. The 95:5 ratio observed in the crystal analyzed by X-ray diffraction was the same ratio found for the entire crop of crystals (bulk sample).

[5] As we reported previously, only ($S_{C\alpha}$)-**4** is observed in NMR spectra recorded at room temperature. Subsequent spectra recorded at low temperature show the presence (8%) of the other fluctional diastereomer, ($R_{C\alpha}$)-**4**. Selected NMR data (CD_2Cl_2, –40°C) for ($S_{C\alpha}$)-**4** and ($R_{C\alpha}$)-**4** (the asterisks denote resonances attributed to the minor diastereomer (($R_{C\alpha}$)-**4**): $^{13}C\{H\}$ NMR (100.6 MHz) δ: 36.1 (s, Ph*C*H$_2$CRu*), 37.8 (s, Ph*C*H$_2$CRu), 66.9 (dd, $^2J_{P(B),C}$ = 42.0 Hz, $^2J_{P(A),C}$ = 3.5 Hz, Ru*C*), 70.0 (dd, $^2J_{P(B'),C}$ = 42.0 Hz, $^2J_{P(A'),C}$ = 3.5 Hz, Ru*C**), 157.9 (br s, *C*O$_2$CH$_3$*), 159.7 (d, $J_{P(B),C}$ = 3.0 Hz, *C*O$_2$CH$_3$), 179.6 (d, $J_{P(B),C}$ = 7.0 Hz, NH*C*OCH$_3$), 179.9 (d, $J_{P(B'),C}$ = 7.0 Hz, NH*C*OCH$_3$*). $^{15}N\{H\}$ NMR INEPT (40.5 MHz) δ: 184.4 (dd, $^2J_{P(A),N}$ = 4.5 Hz, $^2J_{P(B),N}$ = 3.0 Hz, CH$_3$C*N*-Ru). The corresponding ^{15}N resonance for ($R_{C\alpha}$)-**4** was not observed; however, the $^{31}P\{^1H\}$ NMR spectrum of ($R_{C\alpha}$)-**4** prepared using $CH_3C^{15}N$ displayed $^2J_{P(A'),N}$ = 4.5 Hz and $^2J_{P(B'),N}$ = 3.0 Hz. $^{31}P\{H\}$ NMR (161.9 MHz) δ: 32.9 (d, $^2J_{P,P}$ = 23.5 Hz, 1P, P(B)), 40.1 (d, $^2J_{P,P}$ = 24.0 Hz, 1P, P(B′)*), 55.2 (d, $^2J_{P,P}$ = 24.0 Hz, 1P, P(A′)*), 59.4 (d, $^2J_{P,P}$ = 23.5 Hz, 1P, P(A)).

[6] The ee of $MAA(H)_2$ was spectroscopically (^1H NMR) determined using a chiral shift reagent ((+)-Eu(tfc)$_3$) after separation from [Ru((*R*)-BINAP)$(MeCN)_4$]$(BF_4)_2$ by colum chromatography (Florisil–EtOAc). The absolute configuration of the major enantiomer was determined by comparison to authentic (*S*)-$MAA(H)_2$.

Scheme 1.



($S_{C\alpha}$)-**4** as major diastereomer (6). The methyl analogue generated using MAA favours the same absolute configuration as major diastereomer (($S_{C\alpha}$)-**3**), but with a weaker bias (72:28). The protonolysis of these compounds under the described conditions is not stereospecific, and it does not proceed via β-H elimination from the benzyl or methyl groups. Although the lack of observable β-H elimination from the benzyl or methyl groups implies that equilibration of the diastereomers does not occur during the protonolysis, such equilibration may still occur via protonation at the amido nitrogen followed by β-H elimination to form an iminium. These experiments and labeling studies are moot on this point because of rapid proton exchange between the amido group and $HBF_4{\cdot}Et_2O$.

Another explanation for this lack of stereospecificity is that two pathways operate in parallel for the protonolysis. One pathway, resulting in retention at carbon, is protonation at ruthenium followed by elimination of alkane. We note that although there are few examples, all reported electrophilic abstractions of alkyl or vinyl ligands from early or late transition-metal centres by protonolysis occur with retention of configuration at carbon (9). The other pathway, resulting in inversion at carbon, is electrophilic attack at the back side of the Ru–C σ-bond (Scheme 1). Such a possibility has been suggested to account for inversion of configuration at carbon for alkyl abstraction from zirconium complexes by boranes (10), and as discussed in the introduction, for the observed net *anti*-addition of H_2 in certain hydrogenations of olefins (5).

Another explanation for this lack of stereospecificity is prior protonation of a substrate lone pair followed by intramolecular proton transfer. Similar processes have been reported in the literature (cleavage of a Fe–C σ-bond via protonation at nitrogen has been observed, see ref. 11). Scheme 1 shows such a pathway involving protonation of the amido group of MAA(H), followed by a suprafacial intramolecular proton delivery to C(3) with inversion of stereochemistry (intramolecular proton delivery and its role in the reversal of stereochemistry has appeared in the literature, see ref. 12).

Further experimentation (such as low-temperature NMR studies) is required to investigate the stereochemical course of these protonation reactions and their relevance to catalytic hydrogenation of olefins. These results do show, however, that protonolysis of a catalyst–carbon bond is a complicated process, one that should not be assumed a priori to proceed with strict retention.

Experimental

General considerations

All reactions were conducted under an atmosphere of dry Ar (Praxair, 99.998%) using standard Schlenk and glovebox techniques. NMR spectra were recorded using a Bruker AM-400 (^1H at 400.1 MHz, ^2H at 61.4 MHz, ^{13}C at 100.6 MHz, ^{15}N at 40.5 MHz, and ^{31}P at 161.9 MHz) spectrometer. The chemical shifts for ^1H, ^2H, and ^{13}C are reported in parts per million (δ) relative to external TMS and were referenced to residual solvent signals. The chemical shifts for ^{15}N and ^{31}P are reported in parts per million (δ) relative to external liquid NH_3 and external 85% H_3PO_4, respectively. NMR abbreviations used: broad (br), singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet (t), quartet (q), doublet of quartets (dq), doublet of triplets (dt), and multiplet (m). Electron-impact high-resolution mass spectrometry (EI-HRMS) of *N*-acetylalanine methyl ester ($MAA(H)_2$) was performed on a Kratos MS50 spectrometer. Mass spectrometric analysis of **3** (MeCN solution) was performed on a Micromass ZabSpec Hybrid Sector-TOF spectrometer using positive-mode electrospray ionization (ESI-MS (pos)). Calculated *m*/*z* values refer to the isotopes ^{12}C, ^1H, ^{14}N, ^{16}O, ^{31}P, and ^{102}Ru. Microanalyses were performed at the University of Alberta Microanalysis Laboratory.

Materials

Argon gas (Praxair, 99.998%) was dried by passage through a column containing 3 Å molecular sieves and phosphorus pentoxide before use. Dihydrogen gas (Praxair, 99.99%) was passed through an Alltech Oxy-Trap to remove trace amounts of oxygen before use. Dideuterium gas (Aldrich, 99.8%; Praxair, 99.7%) was used as received. All protiated solvents (Anachemia, Caledon, and Fisher Scientific) and deuterated solvents (99.5–99.9% D, Cambridge Isotope Laboratories) were distilled from appropriate drying agents (13) under an atmosphere of argon gas before use except absolute ethanol (200 proof), which was used as received. Unless stated otherwise, all reagents were used as received from Aldrich. [Ru((*R*)-BINAP)(H)(MeCN)$_n$(acetone)$_{3-n}$](BF$_4$) (where n = 0–3) (**2**), **2**-d_1, methyl α-acetamidoacrylate (MAC), [Ru((*R*)-BINAP)(MeCN)((*S*)-MAC(H))](BF$_4$) (($S_{C\alpha}$)-**4** and ($S_{C\alpha}$)-**4**-d_1) were prepared as described previously (6). The ee and absolute configuration of the MAC(H)$_2$-β-d_1 generated from protonolysis of ($S_{C\alpha}$)-**4**-d_1 was determined as described previously (6). Methyl α-acetamidoacrylate (MAA) was purified by column chromatography on neutral alumina (acetone) before use. (*rac*)-MAA(H)$_2$ and (*S*)-MAA(H)$_2$ were prepared by the esterification of (*rac*)-*N*-acetylalanine and (*S*)-*N*-acetylalanine, respectively, using diazomethane (14).

Syntheses

All glassware and syringes were successively treated with ethanolic ammonium hydroxide solution, acetone, and oven-dried before use. Organometallic products were isolated in a glovebox filled with dinitrogen gas and were stored at –30°C for prolonged periods.

3 *and* **3**-d_1

[Ru((*R*)-BINAP)(1–3;5,6-η-C$_8$H$_{11}$)(MeCN)](BF$_4$) (6) (323.9 mg, 0.338 mmol) was partially dissolved in acetone (15.0 mL) under an atmosphere of Ar and subjected to 3 freeze-pump-thaw cycles. The reactor was backfilled with H$_2$ (20 psig, 1 psig = 6.894 kPa) at room temperature and vigorously shaken for 10 min. The resulting orange solution was subjected to 3 freeze-pump-thaw cycles and backfilled with Ar. To this solution at room temperature was added an acetone solution (5.0 mL) of MAA (48.3 mg, 0.338 mmol). The resulting amber solution was shaken for 1 min and the solvent was removed under reduced pressure to give a yellow solid. Dropwise addition of Et$_2$O (80 mL) to a CH$_2$Cl$_2$ (2.0 mL) solution of the product afforded a yellow powder. The product was collected by filtration and washed with Et$_2$O (3 × 10 mL) to yield 310.7 mg (92%) of **3**. NMR spectroscopic analysis showed that the product contained a diastereomeric mixture of ($S_{C\alpha}$)-**3** and ($R_{C\alpha}$)-**3** (72:28). An in situ reaction monitored by NMR spectroscopy displayed the same ratio of diastereomers. The method used for the preparation of **3**-d_1 was the same as that for **3** with substitution of D$_2$ for H$_2$. ESI-MS (pos) *m*/*z*: 909.2 ([M – BF$_4$]$^+$) (exact mass calcd. for C$_{52}$H$_{45}$N$_2$O$_3$P$_2$Ru, 909.2). NMR spectroscopic data for **3** (the asterisks denote resonances attributed to the minor diastereomer (($R_{C\alpha}$)-**3**): ^{1}H NMR (400.1 MHz, (CD$_3$)$_2$CO, 25°C) δ: 1.17 (d, $^4J_{P,H}$ = 5.0 Hz, 3H, RuC-C*H*$_3$*), 1.61 (d, $^4J_{P,H}$ = 5.0 Hz, 3H, RuC-C*H*$_3$), 1.83 (s, 3H, C*H*$_3$CN), 1.92 (s, 3H, C*H*$_3$CN*), 2.04 (s, 3H, NHCOC*H*$_3$), 2.17 (s, 3H, NHCOC*H*$_3$*), 3.77 (s, 3H, CO$_2$C*H*$_3$*), 3.85 (s, 3H, CO$_2$C*H*$_3$), 6.4–8.1 (aromatic), 8.38 (br s, 1H, N*H*COCH$_3$), 9.02 (br s, 1H, N*H*COCH$_3$*). ^{1}H NMR (400.1 MHz, (CD$_3$)$_2$CO, –40°C) δ: 0.99 (d, $^4J_{P,H}$ = 5.0 Hz, 3H, RuC-C*H*$_3$*), 1.55 (d, $^4J_{P,H}$ = 5.0 Hz, 3H, RuC-C*H*$_3$), 1.84 (s, 3H, C*H*$_3$CN), 1.89 (s, 3H, C*H*$_3$CN*), 2.03 (s, 3H, NHCOC*H*$_3$), 2.17 (s, 3H, NHCOC*H*$_3$*), 3.74 (s, 3H, CO$_2$C*H*$_3$*), 3.82 (s, 3H, CO$_2$C*H*$_3$), 6.4–8.1 (aromatic), 8.69 (br s, 1H, N*H*COCH$_3$), 9.28 (br s, 1H, N*H*COCH$_3$*). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 25°C) δ: 4.2 (s, *C*H$_3$CN-Ru*), 4.5 (s, *C*H$_3$CN-Ru), 17.4 (br s, RuC-*C*H$_3$*), 18.8 (s, RuC-*C*H$_3$), 19.7 (s, NHCO*C*H$_3$*), 20.4 (s, NHCO*C*H$_3$), 52.6 (s, CO$_2$*C*H$_3$*), 52.9 (s, CO$_2$*C*H$_3$), 63.3 (dd, $^2J_{P,C(trans)}$ = 44.0 Hz, $^2J_{P,C(cis)}$ = 4.0 Hz, Ru*C*), 66.4 (br d, $^2J_{P,C(trans)}$ = 43.0 Hz, Ru*C**), 126–142 (overlapping aromatic and CH$_3$*C*N), 161.5 (d, $J_{P,C}$ = 3.0 Hz, overlapping ($S_{C\alpha}$)-**3** and ($R_{C\alpha}$)-**3**, *C*O$_2$CH$_3$), 179.3 (d, $J_{P,C}$ = 7.0 Hz, NH*C*OCH$_3$), 179.9 (d, $J_{P,C}$ = 7.0 Hz, NH*C*OCH$_3$*). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, –40°C) δ: 4.1 (s, *C*H$_3$CN-Ru*), 4.3 (s, *C*H$_3$CN-Ru), 16.9 (s, RuC-*C*H$_3$*), 18.2 (s, RuC-*C*H$_3$), 19.5 (s, NHCO*C*H$_3$*), 20.1 (s, NHCO*C*H$_3$), 52.4 (s, CO$_2$*C*H$_3$*), 52.6 (s, CO$_2$*C*H$_3$), 63.0 (dd, $^2J_{P,C(trans)}$ = 43.5 Hz, $^2J_{P,C(cis)}$ = 4.0 Hz, Ru*C*), 66.8 (dd, $^2J_{P,C(trans)}$ = 44.5 Hz, $^2J_{P,C(cis)}$ = 3.0 Hz Ru*C**), 124–141 (overlapping aromatic and CH$_3$*C*N), 159.1 (s, *C*O$_2$CH$_3$*), 160.1 (s, *C*O$_2$CH$_3$), 178.6 (d, $J_{P,C}$ = 7.0 Hz, NH*C*OCH$_3$), 179.1 (d, $J_{P,C}$ = 6.5 Hz, NH*C*OCH$_3$*). ^{15}N NMR INEPT (40.5 MHz, (CD$_3$)$_2$CO, 25°C) δ: 183.1 (dd, $^2J_{P(A),N}$ = 4.5 Hz, $^2J_{P(B),N}$ = 3.0 Hz, CH$_3$C*N*-Ru), 184.8 (dd, $^2J_{P(A),N}$ = 4.0 Hz, $^2J_{P(B),N}$ = 3.0 Hz, CH$_3$C*N*-Ru*). ^{15}N NMR INEPT (40.5 MHz, (CD$_3$)$_2$CO, –40°C) δ: 181.9 (br apparent t, $^2J_{P(A),N}$ = $^2J_{P(B),N}$ = 3.5 Hz, CH$_3$C*N*-Ru), 183.5 (br, CH$_3$C*N*-Ru*). ^{31}P{^{1}H} NMR (161.9 MHz, (CD$_3$)$_2$CO, 25°C) δ: 33.8 (d, $^2J_{P,P}$ = 22.0 Hz, 1P, P(B)), 38.8 (br d, $^2J_{P,P}$ = 21.0 Hz, 1P, P(B′)*), 58.5 (br d, $^2J_{P,P}$ = 21.0 Hz, 1P, P(A′)*), 59.7 (d, $^2J_{P,P}$ = 22.0 Hz, 1P, P(A)). ^{31}P{^{1}H} NMR (161.9 MHz, (CD$_3$)$_2$CO, –40°C) δ: 33.4 (d, $^2J_{P,P}$ = 23.0 Hz, 1P, P(B)), 38.7 (d, $^2J_{P,P}$ = 22.0 Hz, 1P, P(B′)*), 57.1 (d, $^2J_{P,P}$ = 22.0 Hz, 1P, P(A′)*), 59.4 (d, $^2J_{P,P}$ = 23.0 Hz, 1P, P(A)). Anal. calcd. for C$_{52}$H$_{45}$BF$_4$N$_2$O$_3$P$_2$Ru: C 62.72, H 4.56, N 2.81; found: C 62.35, H 4.88, N 2.64.

Protonations of **3** *and* **3**-d_1

To a stirred solution of ($S_{C\alpha}$)-**3** and ($R_{C\alpha}$)-**3** (72:28) (101.0 mg, 0.101 mmol) in CD$_2$Cl$_2$ (0.50 mL) at room temperature was added a solution of HBF$_4$·Et$_2$O (54% w/w in Et$_2$O, 28.0 μL, 0.203 mmol). The originally orange colored solution immediately turned red in color upon addition of HBF$_4$·Et$_2$O. After stirring for 15 min, CD$_3$CN (50.0 μL, 0.957 mmol) was added to the reaction mixture to generate a yellow colored solution. Analysis of the reaction mixture by ^{1}H and ^{31}P NMR spectroscopy indicated that exclusive formation of MAA(H)$_2$ and [Ru((*R*)-BINAP)(CD$_3$CN)$_4$](BF$_4$)$_2$ occurred. The solution was evaporated to dryness and the residue was thoroughly washed with EtOAc (3 × 5 mL) and the wash was passed through a column of Florisil™ (0.5 cm × 7.0 cm). The clear, colorless eluent was evaporated to dryness to give pure MAA(H)$_2$. Protonation of **3**-d_1 exclusively liberated MAA(H)$_2$-β-d_1, as determined by ^{1}H and ^{2}H NMR spectroscopy (^{1}H NMR (400.1 MHz, CDCl$_3$, 25°C) δ: 1.39 (dt, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,D}$ = 2.0 Hz, 2H, CHC*H*$_2$D (Hβ)), 2.02 (s, 3H, NHCOC*H*$_3$), 3.76 (s, 3H,

CO_2CH_3), 4.60 (apparent q, $^3J_{H,H}$ = 7.0 Hz, 1H, C*H*CH_2D (Hα)), 6.05 (br s, 1H, N*H*$COCH_3$). $^2H\{^1H\}$ NMR (61.4 MHz, $CHCl_3$, 25°C) δ: 1.39 (s, $CHCH_2D$)). The enantiomeric excess (ee) and absolute configuration (44% (*S*)) of purified $MAA(H)_2$ and $MAA(H)_2$-β-d_1 were determined as follows. The ee was spectroscopically determined (^1H NMR) using a chiral lanthanide shift reagent (europium tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorate] ((+)-Eu(tfc)$_3$)) in $CDCl_3$. Sufficient shift reagent was added (0.2–0.4 equiv) to separate the methoxy signals (ca. 4 ppm) of the two enantiomers of $MAA(H)_2$ (low-field enantiomer (*R*), high-field enantiomer (*S*)). That these were signals of the enantiomers of $MAA(H)_2$ was confirmed by repeating the experiment using (*rac*)-$MAA(H)_2$. The ratio of these methoxy signals was used to quantify the ee. The absolute configuration of the major enantiomer of the product was determined by addition of authentic (*S*)-$MAA(H)_2$ to the samples and subsequently determining the ee via NMR spectroscopy as described above. Addition of (*S*)-$MAA(H)_2$ caused the intensity of the high-field ((*S*)-enantiomer) methoxy signal to increase.

Deuteriolysis of **3**

In a 5-mm NMR tube, ($S_{C\alpha}$)-**3** and ($R_{C\alpha}$)-**3** (72:28) (10.3 mg, 0.0103 mmol) were dissolved in CD_2Cl_2 (0.50 mL) at room temperature under Ar. The headspace of the NMR tube was thoroughly purged with D_2 and the tube was vigorously shaken. Monitoring the reaction over a 30-min period by ^1H NMR spectroscopy showed the generation of $MAA(H)_2$-α-d_1 (10%) and no detectable incorporation of deuterium in the two diastereomers of **3** (($S_{C\alpha}$)-**3** and ($R_{C\alpha}$)-**3**).

Crystal structure determination of ($S_{C\alpha}$)-3

Slow liquid-liquid diffusion of di-*n*-butyl ether into a 1,2-dimethoxyethane solution of **3** (72:28) at room temperature produced X-ray quality crystals. The structure was determined as described in the supplementary material.[7] Crystal data for ($S_{C\alpha}$)-**3**: $C_{52}H_{45}BF_4N_2O_3P_2Ru$, FW = 995.72, yellow plate, crystal size 0.40 × 0.25 × 0.13 mm, orthorhombic, $C222_1$, a = 21.4849(2), b = 29.7175(2), and c = 18.8513(2) Å, V = 12036.1(2) Å^3, Z = 8, $\rho_{calcd.}$ = 1.099 g cm^{-3}, μ (Mo Kα) = 0.361 mm^{-1}, T = 173(2) K, λ (Mo Kα) = 0.71073 Å. Data were collected using a Siemens SMART Platform CCD diffractometer (θ range for data collection of 1.17–25.04°); 10589 independent reflections (8758 with $F_o^2 > 2\sigma(F_o^2)$) were measured. The structure was solved via direct methods (SHELXTL-V5.0). Full-matrix least-squares refinement on F^2 (SHELXTL-V5.0) yielded R_1 = 0.0480 ($F_o^2 > 2\sigma(F_o^2)$) and wR_2 = 0.1261 (all data). GoF on F^2 = 1.041. Selected bond lengths (Å) and angles (°) with estimated standard deviations for ($S_{C\alpha}$)-**3** are as follows: Ru(1)—N(2) 1.995(4), Ru(1)—P(1) 2.3525(13), Ru(1)—P(2) 2.2640(11), Ru(1)—O(1) 2.072(3), Ru(1)—O(2) 2.278(3), Ru(1)—C(3) 2.230(5), Ru(1)—C(5) 2.345(5), C(3)—C(4) 1.515(7) Å; C(5)-C(3)-C(4) 119.1(4), N(1)-C(3)-C(5) 112.1(4), N(1)-C(3)-C(4) 111.4(4), Ru(1)-C(3)-N(1)101.4(3), Ru(1)-C(3)-C(4) 132.0(3), Ru(1)-C(3)-C(5)76.1(3)°.

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References

1. J. Halpern, J.F. Harrod, and B.R. James. J. Am. Chem. Soc. **83**, 753 (1961).
2. (*a*) B.R. James, D.K.W. Wang, and R. Voigt. J. Chem. Soc. Chem. Comm. 574 (1975); (*b*) B.R. James, A. Pacheco, S.J. Rettig, I.S. Thorburn, R.G. Ball, and J.A. Ibers. J. Mol. Catal. **41**, 147 (1987).
3. (*a*) L.R. Dinelli, A.A. Batista, K. Wohnrath, M.P. de Araujo, S.L. Queiroz, M.R. Bonfadini, G. Oliva, O.R. Nascimento, P.W. Cyr, K.S. McFarlane, and B.R. James. Inorg. Chem. **38**, 5341 (1999); (*b*) N.D. Jones, K.S. MacFarlane, M.B. Smith, R.P. Schutte, S.J. Rettig, and B.R. James. Inorg. Chem. **38**, 3956 (1999); (*c*) N.D. Jones, K.S. MacFarlane, M.B. Smith, R.P. Schutte, S.J. Rettig, and B.R. James. Inorg. Chem. **38**, 3956 (1999); (*d*) K.S. MacFarlane, S.J. Rettig, Z. Liu, and B.R. James. J. Organomet. Chem. **557**, 213 (1998); (*e*) K.S. MacFarlane, I.S. Thorburn, P.W. Cyr, E.K.-Y. Chau, S.J. Rettig, and B.R. James. Inorg. Chim. Acta, **270**, 130 (1998); (*f*) S.L. Queiroz, A.A. Batista, G. Oliva, M.T.D.P. Gambardell, R.H.A. Santos, K.S. McFarlane, S.J. Rettig, and B.R. James. Inorg. Chim. Acta, **267**, 209 (1998); (*g*) B.R. James. Catal. Today, **37**, 209 (1997); (*h*) D.E. Fogg and B.R. James. Inorg. Chem. **36**, 1961 (1997); (*i*) K.S. MacFarlane, A.M. Joshi, S.J. Rettig, and B.R. James. Inorg. Chem. **35**, 7304 (1996); (*j*) D.E.K.Y. Chau and B.R. James. Inorg. Chim. Acta, **240**, 419 (1995); (*k*) D.E. Fogg, S.J. Rettig, and B.R. James. Can. J. Chem. **73**, 1084 (1995); (*l*) D.E. Fogg and B.R. James. Inorg. Chem. **34**, 2557 (1995); (*m*) A.A. Batista, E.A. Polato, S.L. Queiroz, O.R. Nascimento, B.R. James, and S.J. Rettig. Inorg. Chim. Acta, **230**, 111 (1995); (*n*) A.M. Joshi, K.S. MacFarlane, and B.R. James. J. Organomet. Chem. **488**, 161 (1995); (*o*) D.E. Fogg, B.R. James, and M. Kilner. Inorg. Chim. Acta, **222**, 85 (1994); (*p*) A.M. Joshi, I.S. Thorburn, S.J. Rettig, and B.R. James. Inorg. Chim. Acta, **200**, 283 (1992); (*q*) T.W. Dekleva, A.M. Joshi, I.S. Thorburn, B.R. James, S.V. Evans, and J. Trotter. Israel J. Chem. **30**, 343 (1990); (*r*) A.M. Joshi and B.R. James. J. Chem. Soc. Chem. Comm. **22**, 1785 (1989); (*s*) C. Hampton, W.R. Cullen, B.R. James, and J.-P. Charlan. J. Am. Chem. Soc. **110**, 6918 (1988); (*t*) C. Hampton, T.W. Dekleva, B.R. James, and W.R. Cullen. Inorg. Chim. Acta, **145**, 165 (1988); (*u*) I.S. Thorburn, S.J. Rettig, and B.R. James. Inorg. Chem. **25**, 234 (1986); (*v*) B.R. James and D.K.W. Wang. Can. J. Chem.

[7] Supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. For information on obtaining material electronically go to http://www.nrc.ca/cisti/irm/unpub_e.shtml. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

58, 245 (1980); (*w*) B.R. James and D.K.W. Wang. Inorg. Chim. Acta, **19**, L17 (1976) and refs. cited therein.
4. (*a*) M.T. Ashby and J. Halpern. J. Am. Chem. Soc. **113**, 589 (1991); (*b*) T. Ohta, H. Takaya, and R. Noyori. Tetrahedron Lett. **31**, 7189 (1990). Subsequent mechanistic investigations of α,β-unsaturated carboxylic acids have appeared: (*c*) M. Shaharuzzaman, J. Braddock-Wilking, J.S. Chickos, C.N. Tam, R.A.G.D. Silva, and T.A. Keiderling. Tetrahedron: Asymmetry, **9**, 1111 (1998); (*d*) C.-C. Chen, T.-T. Huang, C.-W. Lin, C. Rong, A.C.S. Chan, and W.T. Wong. Inorg. Chim. Acta, **270**, 247 (1998); (*e*) A.C.S. Chan, C.C. Chen, T.K. Yang, J.H. Huang, and Y.C. Lin. Inorg. Chim. Acta, **234**, 95 (1995); (*f*) J.M. Brown, M. Rose, F.I. Knight, and A. Wienand. Recl. Trav. Chim. Pays-Bas. **114**, 242 (1995); (*g*) J.M. Brown. Chem. Soc. Rev. 25 (1993); (*h*) M. Saburi, H. Takeuchi, M. Ogasawara, T. Tsukahara, Y. Ishii, T. Ikariya, T. Takahashi, and Y. Uchida. J. Organomet. Chem. **428**, 155 (1992).
5. F. van Rantwijk and H. van Bekkum. J. Mol. Catal. **1**, 383 (1975/76) and refs. cited therein.
6. (*a*) J.A. Wiles and S.H. Bergens. Organometallics, **18**, 3709 (1999); (*b*) J.A. Wiles and S.H. Bergens. Organometallics, **17**, 2228 (1998); (*c*) J.A. Wiles, S.H. Bergens, and V.G. Young. J. Am. Chem. Soc. **119**, 2940 (1997).
7. *a*) D. Mani, H.-T. Schacht, A.K. Powell, and H. Vahrenkamp. Chem. Ber. **122**, 2245 (1989); (*b*) D. Mani, H.-T. Schacht, A.K. Powell, and H. Vahrenkamp. Organometallics, **6**, 1360 (1987). Structures of other α-metallated amino acids have been reported: (*c*) B. Kayser, C. Missling, J. Knizek, H. Nöth, and W. Beck. Eur. J. Inorg. Chem. 375 (1998); (*d*) B. Kayser, H. Nöth, M. Schmidt, W. Steglich, and W. Beck. Chem. Ber. **129**, 1617 (1996).
8. K. Mashima, T. Hino, and H. Takaya. J. Chem. Soc. Dalton Trans. 2099 (1992).
9. (*a*) E.J. O'Connor, M. Kobayashi, H.G. Floss, and J.A. Gladysz. J. Am. Chem. Soc. **109**, 837 (1987); (*b*) W.N. Rogers and M.C. Baird. J. Organomet. Chem. **182**, C65 (1979); (*c*) M.D. Fryzuk and B. Bosnich. J. Am. Chem. Soc. **101**, 3043 (1979); (*d*) S. Komiya, T. Ito, M. Cowie, A. Yamamoto, and J.A. Ibers. J. Am. Chem. Soc. **98**, 3874 (1976); (*e*) J. Schwartz and J.A. Labinger. Angew. Chem. Int. Ed. Eng. **15**, 333 (1976); (*f*) M.P. Periasamy and H.M. Walborsky. J. Am. Chem. Soc. **97**, 5930 (1975); (*g*) J.A. Labinger, D.W. Hart, W.E. Seibert III, and J. Schwartz. J. Am. Chem. Soc. **97**, 3851 (1975); (*h*) J.F. Normant, G. Cahiez, C. Chuit, and J. Villieras. J. Organomet. Chem. **77**, 269 (1974); (*i*) B.E. Mann, B.L. Shaw, and N. Tucker. J. Chem. Soc. Chem. Commun. 1333 (1970).
10. (*a*) R.E.V.H. Spence, W.E. Piers, Y. Sun, M. Parvez, L.R. MacGillivray, and M.J. Zaworotko. Organometallics, **17**, 2459 (1998); (*b*) X. Yang, C.L. Stern, and T.J. Marks. J. Am. Chem. Soc. **116**, 10015 (1994).
11. Y.-R. Hu, T.W. Leung, S.-C. H. Su, A. Wojcicki, M. Calligaris, and G. Nardin. Organometallics, **4**, 1001 (1985).
12. H.E. Zimmerman and A. Ignatchenko. J. Am. Chem. Soc. **120**, 12992 (1998).
13. (*a*) J. Leonard, B. Lygo, and G. Procter. Advanced practical organic chemistry. 2nd ed. Chapman & Hall, London. 1995; (*b*) Experimental organometallic chemistry: a practicum in synthesis and characterization. *Edited by* A.L. Wayda and M.Y. Darensbourg. ACS Symposium Series 357, American Chemical Society, Washington, DC. 1987.
14. (*a*) J. Leonard, B. Lygo, and G. Procter. Advanced practical organic chemistry. 2nd ed. Chapman & Hall, London. 1995. pp. 103–106; (*b*) B.D. Vineyard, W.S. Knowles, M.J. Sabacky, G.L. Bachman, and D.J. Weinkauff. J. Am. Chem. Soc. **99**, 5946 (1977).