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Reactivity of Molybdenum and Rhenium Hydroxo Complexes toward Organic Electrophiles: Reactions that Afford Carboxylato Products[§]

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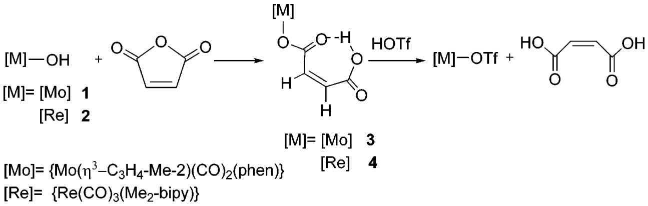
The reactions of the hydroxo complexes [Mo(OH)(η^3-methallyl)(CO)$_2$(phen)] (**1**) and [Re(OH)(CO)$_3$(Me$_2$-bipy)] (**2**) (phen = 1,10-phenanthroline, Me$_2$-bipy= 4,4′-dimethyl-2,2′-bipyridine) with maleic anhydride, phenyl(ethyl)ketene, diphenylketene, and *rac*-lactide afford new carboxylato complexes. The molybdenum and rhenium hydroxo complexes react in the same way, and their reactions are quantitative. The products, some of which have been characterized by X-ray diffraction, feature monodentate O-bonded carboxylato ligands, and their treatment with triflic acid yields the triflato complexes [Mo(OTf)(η^3-methallyl)(CO)$_2$(phen)] and [Re(OTf)(CO)$_3$(Me$_2$-bipy)] and the corresponding free carboxylic acid.

Introduction

Organometallic hydroxo complexes have attracted considerable interest due to their participation in industrially or biologically relevant processes, their rich coordination chemistry, and the challenge of their synthesis.[1] Hydroxo, alkoxo, or amido groups are strongly π-donor ligands. As a result, most complexes with these ligands are found with early transition metals and are stabilized by the ligand-to-metal electron donation. In contrast, late transition metal organometallic complexes with terminal hydroxo ligands are rare, a fact initially attributed to an inherent thermodynamic instability and that now seems rather related to synthetic difficulties and their tendency to oligomerize. Recently, we have found that the easily prepared and relatively stable complexes [Mo(OH)(η^3-methallyl)(CO)$_2$(phen)] (**1**)[2] and [Re(OH)(CO)$_3$(Me$_2$-bipy)] (**2**)[3] show a rich OH-centered reactivity toward organic electrophiles, comparable to that found for hydroxo complexes of groups 8−10.[3c,4] We have previously studied their reactivity toward carbon disulfide, esters, isocyanate, isothiocyanate, and dimethylacetylenedicarboxylate. Reactivity studies of organometallic hydroxo complexes are still very rare. Thus, as an extension of this work, here we report the reactivity of the mentioned hydroxo complexes toward four different carboxylic acid derivatives: a cyclic anhydride, two ketenes, and a lactide. As it will be discussed, the hydroxo complexes act as nucleophiles toward the organic reagents, and the products of such reactions are monodentate carboxylato products; therefore, this study is closely related to those previously carried out by other groups on the reactions of carbon dioxide with alkoxo complexes. Thus, Mandal, Ho, and Orchin reported the reactivity of *fac*-[Mn(OCH$_3$)(CO)$_3$(dppe)],[5] Darensbourg and co-workers conducted a kinetic study on this reaction,[6] and Simpson and Bergman studied the reactivity of analogous rhenium complexes.[7]

Scheme 1. Reaction of the Hydroxo Complexes 1 and 2 with Maleic Anhydride, and Demetalation of the Products by Reaction with Triflic Acid



Results and Discussion

The molybdenum hydroxo complex **1** reacted instantaneously with an equimolar amount of maleic anhydride in THF. The red color of the solution faded upon reaction, and the ν(CO) bands (1929 and 1843 cm^{-1} for **1**) shifted to higher wavenumber values (1957 and 1876 cm^{-1} for the product). The IR of the resulting solution indicates the formation of a single molybdenum *cis*-dicarbonyl compound as product. The shift to higher ν(CO) IR bands reflects a lowering of the electron density at the metal center, as expected for the reaction with an electrophile. The product [Mo(η^3-methallyl){OC(O)CH═CHC(O)-

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[§] Dedicated to Professor Victor Riera on the occasion of his 70th birthday.

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(1) (a) Bryndza, H.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (b) Gilje, J. W.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 895. (c) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44.

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10.1021/om051081g CCC: $33.50

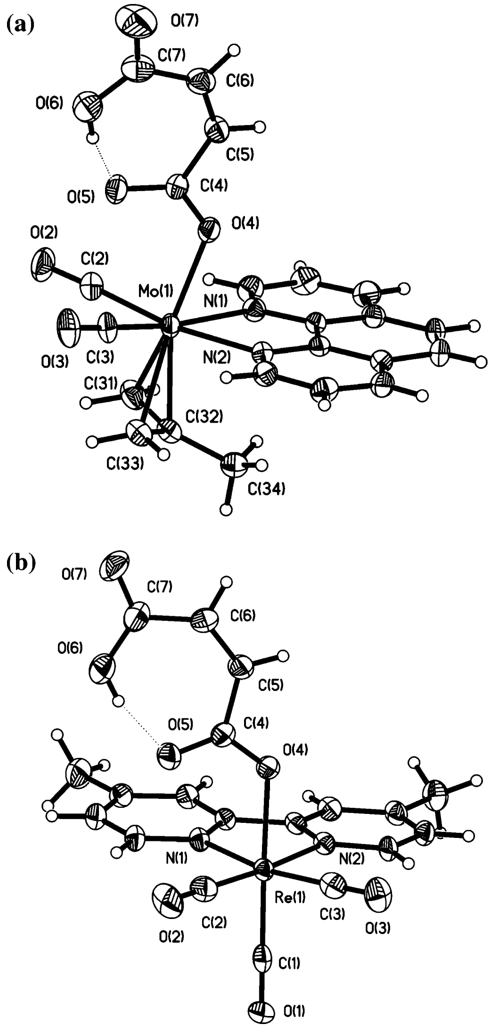


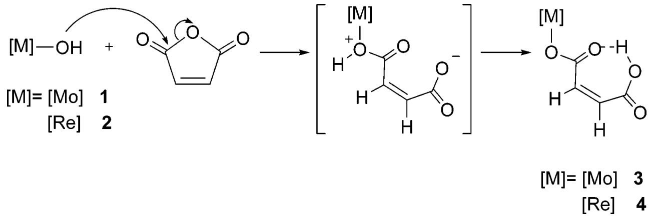
Figure 1. (a) Thermal ellipsoid (30%) plot of **3**. (b) Thermal ellipsoid (30%) plot of **4**.

OH}(CO)$_2$(phen)] (**3**) could be isolated (83%) as a spectroscopically and analytically pure solid by in vacuo concentration followed by precipitation with hexane. The ^{1}H and ^{13}C NMR spectra indicate that the presence of a molecular mirror plane is kept in the product. The ^{1}H NMR spectrum features an AB quartet ($\delta_A = 5.34$, $\delta_B = 5.95$, $J = 12.9$ Hz), assigned to the olefinic hydrogens of a ring-opened product, as depicted in Scheme 1.

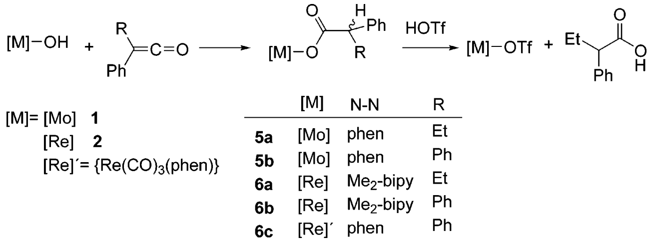
In the ^{13}C NMR, the olefinic carbon atoms appear as low-intensity signals at 132.9 and 130.0 ppm. The solid-state structure of **3** was determined by X-ray diffraction on a single crystal grown by slow diffusion of hexane into a concentrated dichloromethane solution. The results are in agreement with the spectroscopic data mentioned above. A thermal ellipsoid plot is shown in Figure 1a.[8]

The molecule of **3** consists of a hydrogen maleate ligand coordinated through one of the oxygens of the fully deprotonated carboxylate group to a *cis*-{Mo(η^3-methallyl)(CO)$_2$(phen)} fragment. As typically found,[9] an intramolecular hydrogen bond determines a ring-closed structure for the hydrogen maleate ligand. The hydrogen atom involved in this hydrogen bond could be fully refined, and the distances O···O = 2.459 Å and H···O = 1.573 Å and the O−H···O angle = 168.78(2)° indicate a strong hydrogen bond. In the ^{1}H NMR spectrum, this hydrogen appears as a singlet at 16.74 ppm.

Scheme 2. Proposed Mechanism for the Reaction of the Hydroxo Complexes with Maleic Anhydride



Scheme 3. Reaction of the Hydroxo Complexes with Phenyl(ethyl)ketene and Diphenylketene, and Reaction of the Products 5a and 6a with Triflic Acid, Affording the Triflato Complexes and 2-Phenylbutyric Acid



	[M]	N-N	R
5a	[Mo]	phen	Et
5b	[Mo]	phen	Ph
6a	[Re]	Me$_2$-bipy	Et
6b	[Re]	Me$_2$-bipy	Ph
6c	[Re]´	phen	Ph

The rhenium hydroxo complex **2** reacted with maleic anhydride in CH$_2$Cl$_2$ in a similar way, affording the hydrogen maleate product [Re{OC(O)CH=CHC(O)OH}(CO)$_2$(Me$_2$-bipy)] (**4**), which has been isolated in 86% yield and characterized by microanalysis, spectroscopy, and X-ray diffraction (Figure 1b). The reaction was accompanied by a change in color from orange to pale yellow and, as for the molybdenum complexes discussed above, by a shift to higher IR ν(CO) values (1907, 1898, and 1878 cm^{-1} for **2**, 2026, 1925, and 1903 cm^{-1} for **4**). The most informative ^{1}H NMR features are the AB system corresponding to the olefinic hydrogens ($\delta_A = 5.88$, $\delta_B = 5.94$, $J = 12.8$ Hz) and the COOH singlet at 16.43 ppm.

A similar reaction of a hydroxo complex with maleic anhydride has been published by Woerpel and Bergman,[10] and reactions of maleic anhydride with metal alkoxo complexes have been studied by the groups of Bergman and Boncella.[11] A mechanistic proposal, in line with these precedents and with our recent work,[3c] is shown in Scheme 2.

Complexes **3** and **4** do not react with the hydroxo precursors **1** and **2**. The involvement of the carboxylic hydrogen in the intramolecular hydrogen bond can be responsible for the diminished acidity of the COOH groups of **3** and **4**.

CDCl$_3$ solutions of complexes **3** and **4** were allowed to react with equimolar amounts of triflic acid in 5 mm NMR tubes. The ^{1}H NMR spectra showed that both reactions were instantaneous and quantitative, affording the triflato complexes [Mo(OTf)(η^3-methallyl)(CO)$_2$(phen)][12] and [Re(OTf)(CO)$_3$(Me$_2$-bipy)][13] and maleic acid, identified by a singlet at 6.43 ppm (Scheme 1).

The hydroxo complexes **1** and **2** react with phenyl(ethyl)ketene as shown in Scheme 3. The products are the carboxylato

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[8] Full X-ray data are given in the Supporting Information as CIF.

[9] Modec, B.; Brencic, J. V. *Inorg. Chem. Commun.* **2004**, *7*, 516, and references therein.

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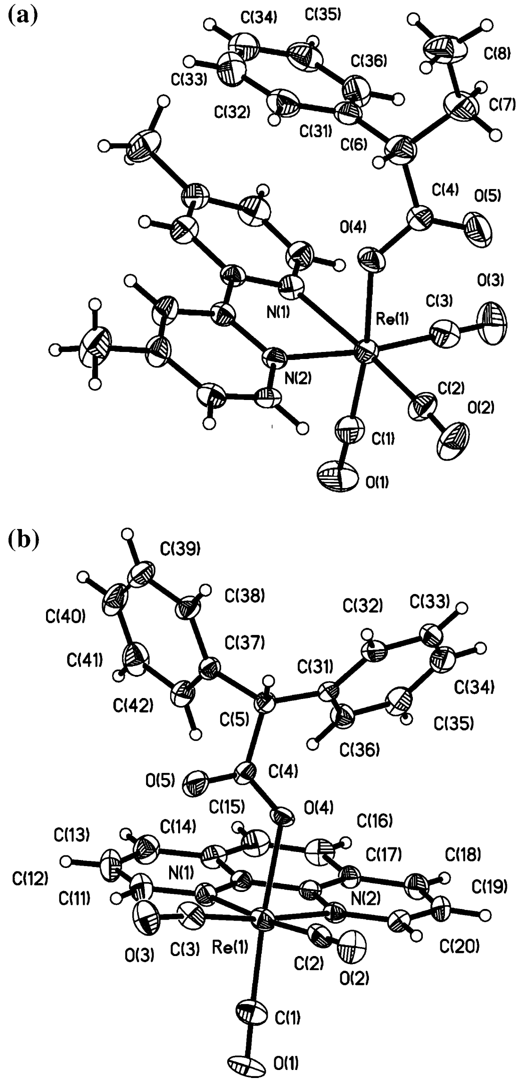
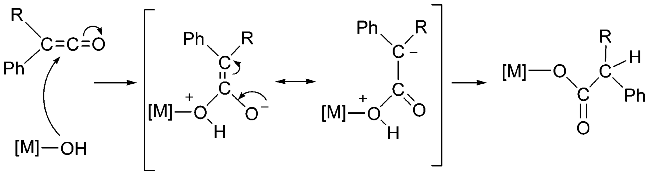


Figure 2. (a) Thermal ellipsoid (30%) plot of **6a**. (b) Thermal ellipsoid (30%) plot of **6c**.

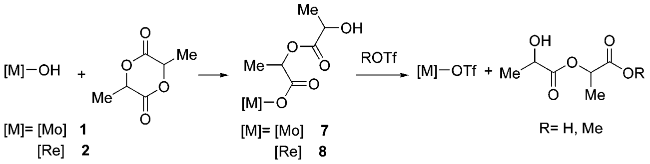
(2-phenylbutyrato) complexes [Mo(η^3-C_3H_4-Me-2){OC(O)CH(Ph)(Et)}(phen)$(CO)_2$] (**5a**) and [Re{OC(O)CH(Ph)(Et)}(Me_2-bipy)$(CO)_3$] (**6a**), which were isolated in yields of 85% and 74%, respectively, resulting from the formal insertion of the ketene into the O−H bond. The addition of excess ketene does not change the nature of the products; thus, a single insertion is observed,[14] as expected since the lone pairs on the metal-bonded oxygen atom of **5a** and **6a** are stabilized by resonance and, therefore, lack nucleophilic character.

Both compounds feature, as expected, IR ν(CO) bands higher than those of the hydroxo precursors. In the ^{1}H NMR in deuterated acetonitrile, the presence of a stereogenic center in the molybdenum complex **5a** breaks the symmetry of the methallyl and phen signals, the two diasterotopic methylene hydrogens appear as two multiplets at 0.63 and 0.51 ppm, and the one-hydrogen signal at 2.69 ppm, corresponding to the hydrogen atom bonded to the stereogenic carbon, appears as a double doublet.[15] The solid-state structure of **5a** was determined by X-ray diffraction, and the results, although of poor quality, are in accord with the solution data and confirm the conectivity of the molecule as depicted in Scheme 3. In the ^{1}H NMR spectrum of the rhenium complex **6a**, the presence of the stereogenic center gives rise to a splitting of the Me_2bipy signals, and the diasterotopic methylene hydrogens appear as two multiplets at 1.75 and 1.32 ppm. The structure of **6a** was determined by X-ray diffraction, and a thermal ellipsoid plot is shown in Figure 2a.[8]

Scheme 4. Proposed Mechanism for the Reactions of 1 and 2 with Phenyl(ethyl)ketene and Diphenylketene



Scheme 5. Reaction of the Hydroxo Complexes 1 and 2 with Lactide, and Reactivity of the Products 7 and 8 toward HOTf and MeOTf



Analogous reactions took place with diphenylketene (see Scheme 3). The products [Mo(η^3-C_3H_4-Me-2){OC(O)CH$(Ph)_2$}(phen)$(CO)_2$] (**5b**) and [Re{OC(O)CH$(Ph)_2$}(Me_2-bipy)$(CO)_3$] (**6b**) were isolated in high yield (88% and 81%, respectively) and characterized by means of microanalysis and IR and NMR spectroscopies. The ^{1}H NMR spectra of **5b** and **6b** showed signals for symmetric phen or Me_2-bipy ligands in accordance with the presence of a molecular mirror plane. All our attempts to obtain single crystals of **6b** suitable for X-ray diffraction were unsuccessful. However, we found that the phen complex [Re{OC(O)CH$(Ph)_2$}(phen)$(CO)_3$] (**6c**), prepared in a completely analogous manner and whose spectroscopic data support a structure like that of **6b** (see Experimental Section), afforded X-ray quality crystals, one of which was used for the determination of the structure (see Figure 2b).

We are not aware of previously reported reactions of hydroxo complexes with ketenes, and our recent reports of the reactivity of ketenes with rhenium amido[16] and alkylideneamido[17] complexes containing metal fragments similar to these included here seem to be the more closely related examples.[18] Scheme 4 displays a mechanistic rationale for the reactions, consisting of nucleophilic attack by the undissociated hydroxo group to generate a zwitterionic intermediate followed by a H^+ migration from the positively charged oxygen to the negatively charged carbon.

Complexes **5a** and **6a** were treated with equimolar amounts of HOTf in $CDCl_3$, and ^{1}H NMR monitoring of the reactions indicated the instantaneous and quantitative formation of the triflato complexes [Mo(OTf)(η^3-methallyl)$(CO)_2$(phen)][12] and [Re(OTf)$(CO)_3$(Me_2-bipy)][13] along with 2-phenylbutyric acid, as depicted in Scheme 3.

The hydroxo complexes **1** and **2** react with *rac*-lactide as indicated in Scheme 5.

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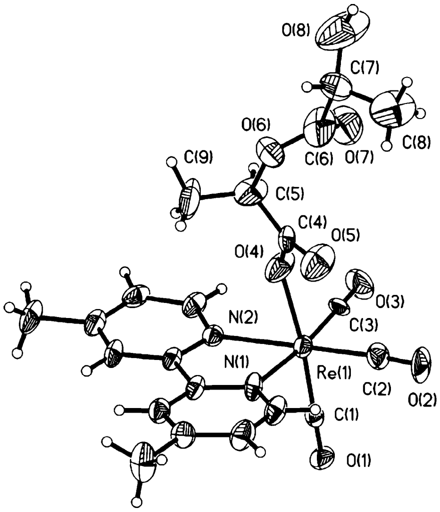
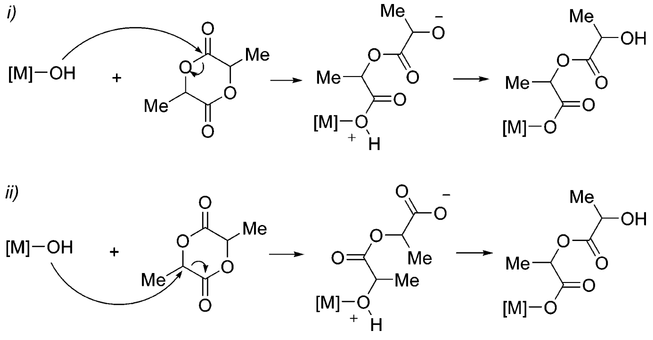


Figure 3. Thermal ellipsoid (30%) plot of [Re{OC(O)C(Me)OC(O)C(Me)OH}(Me$_2$-bipy)(CO)$_3$] (**8**).

Scheme 6. Proposed Mechanisms for the Reaction of the Hydroxo Complexes with Lactide



The IR spectra of the products, [Mo(η^3-C$_3$H$_4$-Me-2){OC(O)C(Me)OC(O)C(Me)OH}(phen)(CO)$_2$] (**7**) and [Re{OC(O)C(Me)OC(O)C(Me)OH}(Me$_2$-bipy)(CO)$_3$] (**8**), showed the expected increase in the wavenumber values of the carbonyl stretching bands. The ^{1}H NMR spectra featured, in addition to the signals of the chelate ligand, the expected two CH quartets and two CH$_3$ doublets for the resulting carboxylato (lactyl-lactato) ligand. The ^{13}C NMR spectrum could be acquired for the more soluble product **8** and was consistent with the formulation given in Scheme 5. The structure of **8** was confirmed by X-ray diffraction, and the thermal ellipsoid plot is shown in Figure 3.[8]

We are not aware of previous reports of stoichiometric reactions between lactides and transition metal hydroxo complexes, in contrast with the extensive studies conducted on the polymerization of lactides initiated by main group complexes.[19] Complexes **7** and **8** do not react with excess lactide.

Scheme 6 shows the two possible mechanisms that can be considered for the reaction, by analogy with proposals made in the context of the mentioned studies of the main group compounds.

Complexes **7** and **8** react with HOTf, affording the triflato complexes [Mo(OTf)(η^3-methallyl)(CO)$_2$(phen)][12] and [Re(OTf)(CO)$_3$(Me$_2$-bipy)][13] along with an equivalent of lactyllactic acid, while employment of MeOTf instead afforded methyl lactyl-lactate, as shown in Scheme 5.

In summary, the hydroxo complexes [Mo(OH)(η^3-methallyl)(CO)$_2$(phen)] (**1**) and [Re(OH)(CO)$_3$(Me$_2$-bipy)] (**2**) react with maleic anhydride, phenyl(ethyl)ketene, diphenylketene, and *rac*-lactide. The reactions are quantitative, affording metal-carboxylate products consistent with initial nucleophilic attack by the OH ligand. The products were characterized by spectroscopy, X-ray diffraction, and demetalation of the corresponding carboxylic acids upon reaction with HOTf. From the synthetic point of view, the chemistry reported here offers a new method to access monodentate carboxylato complexes using reagents soluble in organic solvents, reactions that proceed under mild conditions, and clean processes without side-products.

Experimental Section

General conditions were given elsewhere.[3c] The hydroxo complexes **1**[2] and **2**,[3] phenyl(ethyl)ketene,[20] and diphenylketene[21] were prepared according to literature procedures. Other reagents were purchased and used as received. ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR spectra were recorded on a Bruker Advance 300, DPX-300, or Advance 400 spectrometer. Elemental analyses were carried out on a Fisons EA-1108 analyzer (C, H, and N) at the analytical services of the Universidad de Vigo (Vigo, Spain).

Crystal Structure Determination. General Description. Compounds **3** and **8**: A crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite-monochromatized Mo Kα X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to $2\theta = 48.6°$. Raw frame data were integrated with the SAINT[22] program. An empirical absorption correction was applied with the program SADABS.[23] Compounds **4**, **6a**, and **6c**: Data collection was carried out on a Nonius Kappa CCD single-crystal diffractometer, using Cu Kα radiation. Images were collected at a 29 mm fixed crystal−detector distance, using the oscillation method, with 2° oscillation and 60 s exposure time per image. Data collection strategy was calculated with the program Collect.[24] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[25] Unit cell dimensions were determined from reflections between $\theta = 2°$ and 70°. A semiempirical absorption correction was applied using the program SORTAV.[26] Structure solution and refinement (all): The structures were solved by direct methods with SHELXTL.[27] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter. Calculations were made with SHELXTL and PARST.[28]

Compounds **3** and **6a** crystallize in non-centrosymmetric space groups. Statistics on normalized factors calculated during the data reduction process suggested an acentric distribution of intensities, which was confirmed in the refinement stage. The Flack parameter[29]

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was estimated from experimentally measured Friedel pairs and refined to a value close to 0 for both compounds (0.00(3) from 1253 Friedel pairs for compound **3**; −0.002(18) from 1884 Friedel pairs for compound **6a**).

Synthesis of [Mo(η^3-C_3H_4-Me-2){OC(O)CH═CHC(O)OH}(phen)$(CO)_2$] (3). Maleic anhydride (0.013 g, 0.13 mmol) was added to a solution of **1** (0.050 g, 0.12 mmol) in THF (15 mL). Immediately, the color of the solution changed from deep red to light red. The solution was stirred for 15 min and filtered through diatomaceous earth. In vacuo concentration and addition of hexane (15 mL) caused the precipitation of a red microcrystalline solid, which was washed with hexane (3 × 10 mL) and dried under vacuum. By slow diffusion of hexane into a concentrated solution of **3** in CH_2Cl_2 red needles were obtained, one of which was used for an X-ray analysis. Yield: 0.050 g, 83%. Anal. Calcd for $C_{22}H_{18}MoN_2O_6$: C, 52.60; H, 3.61; N, 5.57. Found: C, 52.66; H, 3.82; N, 5.30. IR (THF): 1957vs, 1876vs (ν_{CO}). ^1H NMR (CD_2Cl_2): 16.74 [s, 1H, C(O)O*H*], 9.36 [m, 2H, phen], 8.57 [d (7.9 Hz), 2H, phen], 8.00 [s, 2H, phen], 7.91 [m, 2H, phen], 5.34, 5.95 [AB (12.9 Hz), 2H, *H*C═C*H*], 3.17 [s, 2H, H_{syn}], 1.44 [s, 2H, H_{anti}], 0.82 [s, 3H, η^3-C_3H_4(C*H*$_3$)-2]. ^{13}C NMR (CD_2Cl_2): 223.1 [2×*C*O], 172.1, 165.8 [2×*C*(O)O], 152.5, 149.9, 138.4,135.6 [phen], 132.9, 130.0 [H*C*═*C*H], 127.4, 124.8 [phen], 81.1 [C_2 of allyl], 54.3 [C_1 and C_3 of allyl], 18.9 [*C*H$_3$ of allyl].

Synthesis of [Re{OC(O)CH═CHC(O)OH}(Me_2-bipy)$(CO)_3$] (4). Maleic anhydride (0.010 g, 0.10 mmol) was added to a solution of **2** (0.050 g, 0.10 mmol) in CH_2Cl_2 (15 mL). The color of the solution changed instanteously from orange to light yellow. The solvent was removed in vacuo to a volume of 5 mL, and addition of hexane (20 mL) caused the precipitation of a yellow microcrystalline solid, which was washed with hexane (10 mL) and redissolved in CH_2Cl_2 (5 mL). Slow diffusion of diethyl ether into this solution at room temperature afforded yellow crystals of **4**, one of which was employed for an X-ray structure determination. Yield: 0.051 g, 86%. Anal. Calcd for $C_{19}H_{15}ReN_2O_7$: C, 40.07; H, 2.65; N, 4.91. Found: C, 40.36; H, 2.82; N, 5.20. IR (CH_2Cl_2): 2026vs, 1925s, 1903s (ν_{CO}). ^1H NMR (CD_2Cl_2): 16.40 [s, C(O)O*H*], 8.89 [d(5.5 Hz), 2H, Me_2-bipy], 8.00 [d(5.5 Hz), 2H, Me_2-bipy], 5.88, 5.94 [AB (12.8 Hz), 2H, *H*C═C*H*], 2.56 [s, 6H, *Me*$_2$-bipy].^{13}C NMR (CD_2Cl_2): 197.8. [2×*C*O], 194.0 [CO], 172.5, 166.0 [2×*C*(O)O], 155.9, 153.6, 152.9 [Me_2-bipy], 135.2, 133.9 [H*C*═*C*H], 128.4, 124.2 [Me_2-bipy], 21.9 [*Me*$_2$-bipy].

Reactions of 3 and 4 with HOTf. NMR tubes of 5 mm were charged with solutions of **3** (0.024 g, 0.045 mmol) and **4** (0.027 g, 0.045 mmol), respectively, in 0.6 mL of $CDCl_3$ and capped with rubber septa. HOTf (4 μL, 0.045 mmol) was injected in each tube, and the reaction was monitored by ^1H NMR. After 5 min the ^1H NMR spectra showed the 6.43 singlet of maleic acid and the signals of the corresponding triflato complexes [Mo(η^3-C_3H_4-Me-2)(OTf)(phen)$(CO)_2$][12] and [Re(OTf)(Me_2-bipy)$(CO)_3$].[13]

Synthesis of [Mo(η^3-C_3H_4-Me-2){OC(O)CH(Ph)(Et)}(phen)$(CO)_2$] (5a). Ph(Et)C═C═O (0.030 g, 0.20 mmol) was added to a solution of **1** (0.054 g, 0.13 mmol) in THF (15 mL), and the red mixture was stirred for 15 min. The solvent was removed in vacuo, and the residue was washed with diethyl ether (2 × 15 mL). Slow diffusion of hexane into a CH_2Cl_2 solution of **5** at −20 °C afforded red crystals, one of which was used for X-ray analysis. Yield: 0.060 g, 85%. Anal. Calcd for $C_{28}H_{26}MoN_2O_4{\cdot}CH_2Cl_2$: C 54.82, H 4.44, N 4.41. Found: C 54.54, H 4.65, N 4.25. IR (CH_2Cl_2): 1948vs, 1861s (ν_{CO}). ^1H NMR (CD_3CN): 9.13 [m, 2H, phen], 8.62 [m, 2H, phen], 8.04 [s, 2H, phen], 7.84 [m, 2H, phen], 6.45 [m, 5H, Ph], 3.12 [s, 2H, H_{syn}], 2.69 [dd (9.4, 9.1 Hz), 1H, C*H*(Et)], 1.26 [s, 1H, H_{anti}], 1.24 [s, 1H, H_{anti}], 0.87 [s, 3H, C*H*$_3$ of allyl], 0.63 [m, 1H, C*H*$_2$ of Et], 0.51 [m, 1H, C*H*$_2$ of Et], 0.20 [t (7.24 Hz), 3H, C*H*$_3$ of Et]. ^{13}C NMR (CD_2Cl_2): 227.9 [2×*C*O], 177.8 [*C*(O)O], 152.0, 145.4, 143.2, 137.9, 130.5, 127.6, 127.4, 127.2, 125.4, 124.7 [phen and Ph], 81.1 [C_2 of allyl], 56.7 [*C*(H)(Et)(Ph)], 54.1 [C_1 and C_3 of allyl], 27.5 [*C*H$_2$ of Et], 19.6 [*C*H$_3$ of allyl], 12.4 [*C*H$_3$ of Et].

Synthesis of [Mo(η^3-C_3H_4-Me-2){OC(O)CH$(Ph)_2$}(phen)$(CO)_2$] (5b). The reaction is similar to that described above for **5a**, starting from Ph_2C═C═O (0.035 g, 0.18 mmol) and **1** (0.070 g, 0.17 mmol). Yield: 0.090 g, 88%. Anal. Calcd for $C_{32}H_{26}MoN_2O_4$: C 64.22, H 4.38, N 4.68. Found: C 63.92, H 4.05, N, 4.84. IR (CH_2Cl_2): 1953vs, 1872s (ν_{CO}). ^1H NMR ($CDCl_3$): 9.12 [d (4.2 Hz), 2H, phen], 8.35 [dd (8.1, 1.1 Hz), 2H, phen], 7.83 [s, 2H, phen], 7.67 [m, 2H, phen], 6.68 [m, 10H, Ph], 4.51 [s, 1H, *H*CPh$_2$], 2.98 [s, 2H, H_{syn}], 1.36 [s, 1H, H_{anti}], 0.80 [s, 3H, C*H*$_3$ of allyl].

Synthesis of [Re{OC(O)CH(Ph)(Et)}(Me_2-bipy)$(CO)_3$] (6a). Ph(Et)C═C═O (0.030 g, 0.20 mmol) was added to a solution of **2** (0.060 g, 0.12 mmol) in CH_2Cl_2 (15 mL). The color of the solution changed from orange to yellow. The solvent was concentrated in vacuo, and addition of hexane (20 mL) caused the precipitation of a yellow microcrystalline solid, which was washed with diethyl ether (2 × 10 mL) and redissolved in CH_2Cl_2 (10 mL). Slow diffusion of hexane into this solution at −20 °C afforded yellow crystals, one of which was employed for an X-ray structure determination. Yield: 0.057 g, 74%. Anal. Calcd for $C_{25}H_{23}N_2O_5Re$: C 48.61, H 3.75, N 4.53. Found: C 48.69, H 3.61, N 4.49. IR (CH_2Cl_2): 2017vs, 1912s, 1888s (ν_{CO}). ^1H NMR (CD_2Cl_2): 8.83 [m, 2H, Me_2-bipy], 7.67 [s, 1H, Me_2-bipy], 7.60 [s, 1H, Me_2-bipy], 7.29−7.20 [m, 2H, Me_2-bipy], 7.09−6.90 [m, 3H, Ph], 6.63−6.61 [m, 2H, Ph], 2.87 [t (7.6 Hz), 1H, C*H*(Et)(Ph)], 2.51 [s, 3H, Me_2-bipy], 1.75 [m, 1H, *C*H$_2$ of Et], 1.32 [m, 1H, *C*H$_2$ of Et], 0.57 [t (7.2 Hz), 3H, *C*H$_3$ of Et]. ^{13}C NMR (CD_2Cl_2): 201.1, 196.9, 190.8 [1 *C*O each], 179.7 [*C*(O)O], 157.6, 157.3, 155.3, 155.0, 153.7, 153.5 [Me_2-bipy], 145.3, 130.7, 129.9, 129.7 [Ph], 128.3, 127.5 [Ph], 125.7, 125.6 [Me_2-bipy], 58.1 [*C*(H)(Et)(Ph)], 29.1 [*C*H$_2$ of Et], 23.8, 23.7 [*Me*$_2$-bipy], 14.5 [*C*H$_3$ of Et].

Synthesis of [Re{OC(O)CH$(Ph)_2$}(Me_2-bipy)$(CO)_3$] (6b). The procedure was as described for **6a**, using Ph_2C═C═O (0.025 g, 0.13 mmol) and **2** (0.060 g, 0.12 mmol). The color of the solution changed instantaneously from orange to yellow. Yield: 0.054 g, 81%. Anal. Calcd for $C_{29}H_{23}N_2O_5Re$: C 52.32, H 3.48, N 4.21. Found: C 51.99, H 3.33, N 4.17. IR (CH_2Cl_2): 2020vs, 1911s, 1897s (ν_{CO}). ^1H NMR (CD_2Cl_2): 8.87 [d (5.6 Hz), 2H, Me_2-bipy], 7.72 [s, 2H, Me_2-bipy], 7.72 [d (5.6 Hz), 2H, Me_2-bipy], 7.10 [m, 2H, Ph], 7.04 [m, 4H, Ph], 6.87 [m, 4H, Ph], 4.52 [s, 1H, *H*CPh$_2$], 2.51 [s, 3H, Me_2-bipy].

Synthesis of [Re{OC(O)CH$(Ph)_2$}(phen)$(CO)_3$] (6c). The procedure was as described for **6a** and **6b**, using [Re(OH)$(CO)_3$(phen)] (0.060 g, 0.12 mmol) and Ph(Et)C═C═O (0.025 g, 0.13 mmol). The color of the solution changed immediately from orange to yellow. Slow diffusion of hexane into a solution of **6c** in CH_2Cl_2 at room temperature afforded yellow crystals, one of which was suitable for an X-ray analysis. Yield: 0.052 g, 78%. Anal. Calcd for $C_{29}H_{19}N_2O_5Re$: C 52.65, H 2.89, N 4.23. Found: C 52.70, H 3.02, N 4.11. IR (CH_2Cl_2): 2021vs, 1914s, 1904s (ν_{CO}). ^1H NMR (CD_2Cl_2): 9.35 [m, 2H, phen], 8.47 [m, 2H, phen], 7.99 [s, 2H, phen], 7.78 [m, 2H, phen], 6.81 [m, 2H, Ph], 6.77 [m, 4H, Ph], 6.31 [m, 4H, Ph], 4.49 [s, 1H, *H*CPh$_2$].

[Re(OH)$(CO)_3$(phen)] was prepared following the procedure described for [Re(OH)$(CO)_3$(Me_2-bipy)],[3] using [Re(OTf)$(CO)_3$(phen)] (0.200 g, 0.33 mmol) and KOH (0.085 mL of a solution 4 M in H_2O). Yield: 0.132 g, 84%. Anal. Calcd for $C_{15}H_9N_2O_4Re$: C 38.46, H 1.94, N 5.98. Found: C 38.27, H 2.81, N 5.81. IR (CH_2Cl_2): 2009vs, 1899s, 1890s (ν_{CO}). ^1H NMR (CD_2Cl_2): 9.41 [m, 2H, phen], 9.04 [m, 2H, phen], 8.07 [s, 2H, phen], 7.88 [m, 2H, phen], 1.16 [s, 1H, O*H*].

Reactions of 5a and 6a with HOTf. The reactions were conducted as described above for the reactions of **3** and **4** with HOTf. 2-Phenylbutyric acid was identified by comparison with a commercial sample.

Table 1. Crystallographic Data for 3, 4, 6a, 6c, and 8

	3	**4**	**6a**	**6c**	**8**
formula	$C_{22}H_{18}MoN_2O_6$	$C_{19}H_{15}N_2O_7Re$	$C_{25}H_{23}N_2O_5Re$	$C_{29}H_{19}N_2O_5Re$	$C_{21}H_{21}N_2O_8Re$
fw	502.32	569.53	617.65	661.66	615.60
cryst syst	orthorombic	triclinic	orthorombic	triclinico	monoclinic
space group	$P2(1)2(1)2(1)$	$P\bar{1}$	$P2(1)2(1)2$	$P\bar{1}$	$C2/c$
a, Å	10.027(2)	6.2719(13)	14.416(3)	10.380(2)	12.6148(15)
b, Å	10.868(2)	9.939(2)	17.067(3)	10.971(2)	10.8812(13)
c, Å	19.014(4)	16.062(3)	9.793(2)	11.236(2)	32.845(4)
α, deg	90	98.90(3)	90	93.73(3)	90
β, deg	90	96.82(3)	90	95.36(3)	96.889(2)
γ, deg	90	99.61(3)	90	105.83(3)	90
V, Å^3	2072.1(8)	964.4(3)	2409.4(8)	1220.2(4)	4475.9(9)
Z	4	2	4	2	8
T, K	293(2)	293(2)	293(2)	293(2)	299(2)
D_c, g cm^{-3}	1.610	1.961	1.703	1.801	1.827
$F(000)$	1016	548	1208	644	2400
λ(Mo Kα), Å	0.71073	1.54184	1.54184	1.54184	071073
cryst size, mm	0.13 × 0.16 × 0.28	0.30 × 0.10 × 0.05	0.10 × 0.07 × 0.05	0.10 × 0.07 × 0.07	0.14 × 0.37 × 0.41
μ, mm^{-1}	0.675	12.731	10.181	10.110	5.479
scan range, deg	$2.14 \leq \theta \leq 23.28$	$2.82 \leq \theta \leq 68.58$	$4.01 \leq \theta \leq 68.25$	$3.97 \leq \theta \leq 68.23$	$1.25 \leq \theta \leq 23.27$
no. of reflns measd	9153	5014	4399	17 155	9745
no. of indep reflns	2976	3502	2461	4361	3224
no. of data/restraints/params	2976/0/286	3502/0/269	4399/0/302	4064/0/335	3224/0/295
goodness-of-fit on F^2	1.054	1.078	1.030	1.355	1.418
R_1/R_{w2} [$I>2\sigma(I)$]	0.0189/0.0478	0.0379/0.1004	0.0517/0.1302	0.0338/0.0849	0.0694/ 0.1664
$R_1/R_w{}^2$ (all data)	0.0201/0.0485	0.0388/ 0.1015	0.0556/0.1364	0.0369/0.0873	0.0730/ 0.1760

Synthesis of [Mo(η^3-C_3H_4-Me-2){OC(O)C(Me)OC(O)C(Me)-OH}(phen)(CO)$_2$] (7). *rac*-3,6-Dimethyl-1,4-dioxan-2,5-dione (0.022 g, 0.15 mmol) was added to a solution of **1** (0.060 g, 0.15 mmol) in THF (15 mL) and stirred for 12 h. The red solution was filtered through diatomaceous earth, concentrated in vacuo to a volume of 5 mL, and layered with hexane, affording after slow diffusion at room temperature red needles of **7**. Yield: 0.060 g, 80%. Anal. Calcd for $C_{24}H_{24}MoN_2O_7$: C, 52.56; H, 4.41; N, 5.11. Found: C, 52.32; H, 4.60; N, 5.01. IR (THF): 1954vs, 1870vs (ν_{CO}). ^{1}H NMR (CD_2Cl_2): 9.26 [dd (3.5, 1.6 Hz), 2H, phen], 8.54 [dd (6.7, 1.3 Hz), 2H, phen], 7.99 [s, 2H, phen], 7.88 [m, 2H, phen], 4.31 [q (7.1 Hz), 1H, C*H*(CH$_3$)], 3.84 [q (7.1 Hz), 1H, C*H*(CH$_3$)], 3.10 [s, 2H, H_{syn}], 2.46 [s br, 1H, O*H*], 1.83 [s, 2H, H_{anti}], 1.59 [s, 3H, *C*H_3 of allyl], 1.08 [d (7.1 Hz), 3H, CH(*CH*$_3$)], 0.57 [d (7.1 Hz), 3H, CH(*CH*$_3$)].

Synthesis of [Re{OC(O)C(Me)OC(O)C(Me)OH}(Me$_2$-bipy)-(CO)$_3$] (8). *rac*-3,6-Dimethyl-1,4-dioxan-2,5-dione (0.024 g, 0.170 mmol) was added to a solution of **2** (0.080 g, 0.169 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 30 min, and the color of the solution changed from orange to yellow. The solution was concentrated under vacuum to a volume of 10 mL, layered with hexane (20 mL), and stored at −20 °C, affording, after slow diffusion, yellow crystals of **8**, one of which was used for the structure determination by X-ray diffraction. Yield: 0.083 g, 78%. Anal. Calcd for $C_{21}H_{21}N_3O_8Re$: C, 40.97; H, 3.43; N, 4.55. Found: C, 40.63; H, 3.11; N, 4.59. IR (CH_2Cl_2): 2020vs, 1915s, 1891s (ν_{CO}). ^{1}H NMR (CD_2Cl_2): 8.89 [d (5.4 Hz), 2H, Me$_2$-bipy], 7.99 [s, 2H, Me$_2$-bipy], 7.34 [d (5.4 Hz), 2H, Me$_2$-bipy], 4.55 [q (7.1 Hz), 1H, C*H*CH$_3$], 3.94 [q (6.9 Hz), 1H, C*H*CH$_3$], 2.57 [s, 6H *Me*$_2$-bipy], 1.05 [d (7.1 Hz), 3H, CHC*H*$_3$], 1.00 [d (6.9 Hz), 3H, CHC*H*$_3$]. ^{13}C NMR (CD_2Cl_2): 198.9. [2×*C*O], 194.4 [*C*O], 175.0, 174.4 [2×*C*(O)O], 156.0, 153.6, 152.3, 128.0, 124.0 [Me$_2$-bipy], 71.7, 66.8 [2×*C*(CH$_3$)], 21.9 [*Me*$_2$-bipy], 20.2, 17.6 [2×C(*C*H$_3$)].

Reactions of 7 and 8 with 0.9 equiv of HOTf. These reactions were performed in NMR tubes and ^{1}H NMR-monitored, as described above, using **7** (0.022 g 0.038 mmol), **8** (0.024 g, 0.038 mmol), and HOTf (3 μL, 0.034 mmol). After 5 min, the ^{1}H NMR spectra showed signals for lactyl-lactic acid,[30] the corresponding triflato complexes, and small amounts of unreacted **7** or **8**. Less than the stoichiometric amounts of triflic acid had to be used; otherwise, acid-catalyzed cyclization of lactyl-lactic acid to the starting lactide was observed.

Reactions of 7 and 8 with MeOTf. Two 5 mm NMR tubes were charged with solutions of **7** (0.022 g, 0.038 mmol) and **8** (0.024 g, 0.038 mmol) in 0.6 mL of $CDCl_3$ and capped with rubber septa. MeOTf (4 μL, 0.039 mmol) was injected, and the reactions were monitored by ^{1}H NMR. After 1 h (in the case of the molybdenum complex) and 12 h (rhenium complex), the ^{1}H NMR spectra showed signals for free methyl-2-(2-hydroxypropionyl)-propionate[31] and the triflato complexes.

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Supporting Information Available: X-ray crystallographic data for compounds **3**, **4**, **6a**, **6c**, and **8** as CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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