Multiple Bonds between Main-Group Elements and Transition Metals. 135.[1] Oxorhenium(V) Catalysts for the Olefination of Aldehydes

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Reaction of methyltrioxorhenium (MTO) (**1**) and triphenylphosphine in diethyl ether gives bis(triphenylphosphine)methyldioxorhenium(V)·MTO (**3a**), which was characterized by a single-crystal X-ray diffraction study (crystal data: space group *Cc*, $a = 1393.5(4)$ pm, $b = 1367.5(1)$ pm, $c = 1928.0(5)$ pm, $\beta = 102.67(1)°$, $Z = 4$). An MTO molecule acts as an axial Lewis base ligand in this mixed-valence Re^V/Re^{VII} complex that is structurally composed of two trigonal bipyramids joined *via* an unsymmetrical, slightly bent oxo bridge ligand. Both phosphine ligands of the Re^V fragment are in *trans* positions to each other while the methyl and oxo groups occupy equatorial sites. **3a** as well as bis(triphenylphosphine)trichlororhenium(V) (**4**) are used as catalysts for the olefination of aldehydes with diazoalkanes.

Introduction

Recently we reported that methyltrioxorhenium(VII), CH_3ReO_3 (MTO, **1**),[2] is an efficient catalyst in olefin oxidation,[3] olefin metathesis,[4] oxidation of metal carbonyls,[5] and olefination of aldehydes.[6] When aldehydes are treated with certain diazoalkanes in the presence of a tertiary phosphine, the olefin coupling product is formed in the presence of MTO as a catalyst (eq 1).

$$R^1CHO + N_2{=}CR^2R^3 + PR'_3 \xrightarrow{\text{cat. MTO}} R^1{\sim}CH{=}CR^2R^3 + N_2 + O{=}PR'_3 \quad (1)$$

Advantages of this reaction are easily accessible starting materials, facile procedures, mild conditions, and good yields. Diazoacetate and -malonate can thus be converted into olefins containing terminal carboxy groups. MTO thus is the first structurally defined organometallic compound that *catalyzes* aldehyde olefination. This paper describes a well-characterized catalytic intermediate.

Results and Discussion

A. Synthesis and Spectroscopy. While the complex $(\eta^5\text{-}C_5Me_5)ReO_3$[7] reacts with sulfonated or polymer-supported triphenylphosphine to give the reduced dimer $(\eta^5\text{-}C_5Me_5)_2Re_2O_4$ (Re^V) in good yields,[8] a similar behavior of the formally analogous CH_3ReO_3 is not observed. It has previously not been possible to isolate a well-characterized product from CH_3ReO_3/PPh_3. The reaction of **1** with triphenylphosphine in toluene at 25 °C was monitored by ^{31}P NMR spectroscopy. During the reaction the signal of triphenylphosphine decreases ($\delta P = -5.5$ ppm *vs* ext. 85% H_3PO_4), while two new signals appear ($\delta = +9.7, +29.0$ ppm). The latter (29.0 ppm) was reasonably assigned to triphenylphosphine oxide in free or metal-coordinated form, *e.g.*, $CH_3ReO_2{\cdot}OPPh_3$. Addition of an alkyne to a mixture of **1** and polymer-supported triphenylphosphine gives alkyne complexes of type **2**.[9]

We now found that the intermediate **3a** ($\delta = 9.9$ ppm, ^{31}P NMR) is formed when triphenylphosphine is added to the colorless solution of **1** in diethyl ether. The solution immediately turns yellow and slowly changes to red and brown. After approximately 30 min, **3a** starts to precipitate (Scheme 1) as an orange solid that can be stored under nitrogen at room temperature for several weeks. It can briefly be handled in air. However, **3a** quickly decomposes in solvents other than diethyl ether or pentane. The synthesis of type **3** compounds is not generally applicable to phosphines because either there is no precipation of the product (*e.g.*, tris-*n*-butylphosphine) or the resulting product escapes purification. Isolation of clean **3b**, a red powder, was possible (tris(cyclohexyl)phosphine as ligand).

The methyldioxorhenium(V) fragment of **3a,b** is formally a 12e species. Coordination of two phosphine

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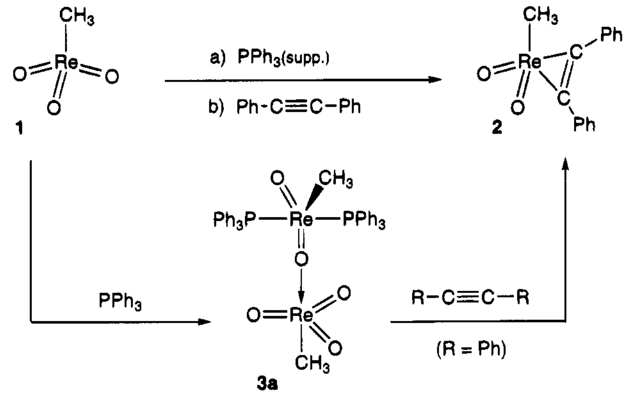
Scheme 1 [a]



[a] Compound **3b** with tris(cyclohexyl)phosphine in place of triphenylphosphine has been obtained analogously

molecules certainly alleviates the electron deficiency of this species. The *trans* configuration of the phosphines appears to be maintained in solution (one signal at δ = 9.9 ppm, ^{31}P NMR). A similar situation is found in the cases of $ReIO_2(PPh_3)_2$[10] and $ReCl_3O(PPh_3)_2$ (**4**)[11] where the rhenium(V) fragment also coordinates two phosphine molecules in a *trans* geometry.

It is known that **1** forms 1/1 adducts especially with N donors like pyridine or quinuclidine.[12] Still, it is surprising that **3a** precipitates with 1 equiv of **1** as a Lewis acid/base adduct, with the rhenium(V) fragment $CH_3ReO_2(PPh_3)_2$ acting as an O donor. Two different methyl groups are seen in the ^{1}H NMR spectra: the signal of the MTO unit (δ = 2.60 ppm [$CDCl_3$] in free MTO) is shifted to higher field as a result of complexation (δ = 1.73 ppm), whereas the methyl group at rhenium(V) has a signal at δ = 3.05 ppm. Since $CH_3ReO_2(PPh_3)_2$ is not expected to be a strong donor with respect to MTO, **3a** is not very stable. In the FAB mass spectra only the mononuclear components CH_3ReO_3 and $CH_3ReO_2(PPh_3)_2$ as well as their fragments are observed. A Re(VII)/Re(V) complex was obtained from reaction of Re_2O_7 with triethylphosphine in pyridine; in the product $[ReO_2(py)_4]^+[ReO_4]^-$ (py = pyridine), the fragment $[ReO_2(py)_4]^+$ is stabilized by four pyridine molecules.[13] In this case, however, no interaction of the Re(V) and the Re(VII) species occurs, so that a true comparison with **3a** is not possible.

3a is an intermediate in the formation of the alkyne complex **2**: an excess of diphenylacetylene reacts in toluene with **3a** to give, after purification by column chromatography, the π-alkyne complex **2** as a yellow powder (Scheme 1). Since the yield of **2** (78% based upon **3a**) exceeds the Re(V) equivalents, one must assume that the free phosphine again reacts with CH_3ReO_3 to give more of the reactive intermediate **3a**.

Table 1. Olefination of Aldehydes Catalyzed by the Rhenium Complexes 1 and 3[a]

aldehyde	**1** (10 mol %) olefin (yield) (%)	**1** (10 mol %) E/Z	**3a** (5 mol %) olefin (yield) (%)	**3a** (5 mol %) E/Z
$4\text{-}O_2NC_6H_4CHO$[b]	93	92/8	89	78/22
$4\text{-}CH_3C_6H_4CHO$[b]	79	76/24	71	70/30
$4\text{-}FC_6H_4CHO$[b]	94	66/34	89	67/33
$4\text{-}FC_6H_4CHO$[c]	93	68/32		
$4\text{-}FC_6H_4CHO$[d]	72	80/20		
$4\text{-}FC_6H_4CHO$[e]	71	60/40		
$4\text{-}FC_6H_4CHO$[f]	84	65/35		
$4\text{-}FC_6H_4CHO$[g]	88	64/36		
$4\text{-}FC_6H_4CHO$[h]	89	64/36		
$CH_3CH_2CH_2CHO$[i]	89	67/33		
$(CH_3)_2CHCHO$[i]	82	85/15		
$(CH_3)_3CCHO$[i]	16	99/1		

[a] Diazo compound, $N_2{=}CHCOOEt$; phosphine, PPh_3; THF. [b] 25 °C; 2 h. [c] 66 °C; 2 h. [d] 35 °C; 24 h. [e] 25 °C; 5 min. [f] 25 °C; 40 min. [g] 25 °C; 100 min. [h] 25 °C; 160 min. [i] 25 °C, 5 h.

B. Catalysis. An equimolar mixture of aldehyde, diazoalkane, and triphenylphosphine gives an olefin coupling product if **1** is used as catalyst.[6] Saturated and α,β-unsaturated aldehydes as well as benzaldehyde and its derivatives are preferred substrates. Electron-withdrawing substituents favor this reaction. Here we introduce new mechanistic aspects and an improvement of the aldehyde olefination.

Compound **3a** reacts in the absence of triphenylphosphine with a stoichiometric amount of 4-nitrobenzaldehyde and an excess of ethyl diazoacetate; the olefinic coupling product $4\text{-}NO_2C_6H_4CH{=}CHCOOEt$ (*E* and *Z* isomers) forms quantitatively (based on aldehyde), together with small amounts of the byproduct $EtOOCCH{=}CHCOOEt$ (*E*/*Z* isomer). Triphenylphosphine oxide, **1**, and some still unidentified brown oil (caused by decomposition of **3a** during the reaction) were also obtained (eq 2). With catalytic amounts of **3a** (5 mol %; 25 °C; 2 h), the yields of olefins are in the range of 70–90% (Table 1) when a phosphine is present.

$$\mathbf{3a} + 4\text{-}O_2NC_6H_4CHO + N_2CHCOOEt \xrightarrow[\text{THF}]{-N_2} 4\text{-}O_2NC_6H_4CH{=}CHCOOEt + EtOOCCH{=}CHCOOEt + O{=}PPh_3 + MTO \quad (2)$$

The phenomena of the aldehyde olefination catalyzed by **3a** are similar to those of the same reaction catalyzed by **1**/PPh_3. Both **1** and **3a** are more effective for aryl aldehyde having an electron-withdrawing group in the *para* position of the benzene ring. The olefination of these aryl aldehydes results in higher yields than those having electron-donating groups in the *para* position. When the catalyst **3a** was less than 2 mol %, the yields of olefins decreased and larger amounts of azines $RCH{=}NN{=}CHR'$ occured (30–35%) (the R group originates from the diazoester).

Temperature, initial amount of catalyst, as well as the structure of aldehyde and diazoalkane, influence the *cis*/*trans* selectivity for cinnamates. *trans*-Cinnamates preferentially are formed at low temperature (Table 1). The stoichiometric reaction of **3a** with 4-fluorobenzaldehyde and ethyl diazoacetate affords more *cis*- than *trans*-olefins. A decreasing amount of catalyst increases the *trans*/*cis* ratio but also lowers the yield of olefins as a result of increasing formation of azines $RCH{=}N\text{-}N{=}CHR'$ that become the main products when the

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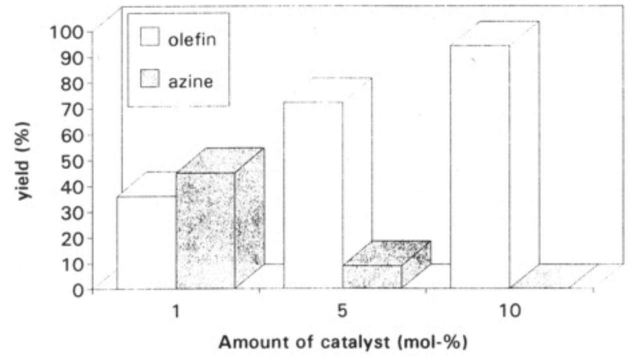

Figure 1. Aldehyde olefination catalyzed by **1** with different amounts of catalyst: aldehyde, 4-FC_6H_4-CHO; diazo compound, N_2=CHCOOEt; phosphine, PPh_3; azine compound, RCH=NN=CHR′ (R = 4-FC_6H_4CH, R′ = CHCOOEt); THF; 25 °C; 4 h.

initial amount of **1** is only 1 mol % (Figure 1). Bulky aldehydes improve the selectivity for *trans*-olefins drastically (Table 1). The *cis*/*trans* ratio does not change with the reaction time. Even after refluxing the reaction solution for several hours in toluene, no isomerization occurs.

A disadvantage of the (isolated) catalyst **3a** is fast decomposition in solution to give **1**, CH_4 (gas-phase GC analysis), and an uncharacterized brown perrhenate compound. *In situ* preparation from CH_3ReO_3 and PPh_3 gives a more efficient catalyst. We found that the known Re(V) compound **4** is active, too. By way of contrast, coordinatively saturated Re(VII) complexes such as (η^5-C_5H_5)ReO_3, (η^5-C_5Me_5)ReO_3, and (4,4′-di-*tert*-butyl-2,2′-bipyridine)·MTO are far less active than **1**, **3a**, or **4**. Compounds without oxo groups such as (η^5-C_5Me_5)$Re(CO)_3$, $BrRe(CO)_5$, $Re_2(CO)_{10}$, and perrhenates (*e.g.*, $[NH_4][ReO_4]$, $Me_3SnOReO_3$) are completely inactive in aldehyde olefinations of eq 1.

We assume that the mechanistic characteristics of the catalysis of **4** in the presence of triphenylphosphine are similar to that of the reaction catalyzed by **1**. It is probable that one triphenylphosphine in **4** is replaced by an aldehyde. This is in accordance with the known complex $[ReOCl_3(O(CH)NMe_2)(PPh_3)]$, where instead of one triphenylphosphine DMF is bound via an oxygen to the rhenium center.[14] Although **4** is only slightly soluble in THF, both the yields and *trans*/*cis* selectivity are higher than for other rhenium complexes tested so far, including **1** (Table 2). Catalyst **4** is more stable than **3a**, thus being more resistant to decomposition.

C. Crystallography. The crystal structure of the mixed-valence complex **3a** is best described as two oxo-bridged corner-sharing trigonal bipyramids (Figure 2). The unprecendented type of $Re^{V}-O-Re^{VII}$ bridge is slightly bent (162.2(4)°), and the bonding geometry ($Re^{V}=O$ 175.4(8) and $O\rightarrow Re^{VII}$ 237.7(7) pm) is highly asymmetric. The structure of the MTO moiety resembles the trigonal-bipyramidal structures of known N donor adducts of MTO. In nearly all cases the methyl group and the donor ligand are located in axial positions while the oxo groups occupy the equatorial sites.[3c] The $Re^{VII}-C$ distance of 203(1) pm is remarkably short as compared with the data of N donor adducts of compounds $R-ReO_3$ ($R-ReO_3$·quinuclidine, 207(1)-210.5(4) pm;[15] *trans*-CH_3ReO_3·aniline, 209.5(5)) pm;[12] CH_3ReO_3·toluidine, 210(1) pm;[16] CH_3ReO_3·4-butylpyridine, 208.5(6) pm[17]). Also, the Re—C bond distance of MTO itself (neutron powder diffraction, 206.3(2) pm; gas-phase electron diffraction, 206.0(9) pm)[18] and of the highly Lewis acidic peroxo complex $CH_3Re(O_2)_2O$ (204(1) pm; gas-phase electron diffraction)[19] are in the same range. The Lewis basicity of the $Re^{V}=O$ moiety is, as expected, quite low as compared with that of N donor ligands. The $Re^{V}-C$ distance amounting to 211(1) pm is in the same range as $Re^{VII}-C$ distances of N donor adducts of $R-ReO_3$ (R = alkyl, see above).

Table 2. Aldehyde Olefination Catalyzed by Rhenium Oxo Complexes[a]

catalyst	mol %	olefin yield (%)	*E*/*Z*
1	10	94	66/34
	5	72	93/7
	1	36	92/8
3a	10	95	59/41
	5	89	67/33
	1	29	88/12
4	10	100	90/10
	5	99	91/9
	1	90[b]	94/6

[a] Aldehyde, 4-FC_6H_4CHO (1.0 mmol); diazo compound, N_2=CHCOOEt (1.4 mmol); PPh_3 (1.0 mmol). The yields were determined by GC. [b] Isolated yield; aldehyde, 4-$O_2NC_6H_4CHO$.

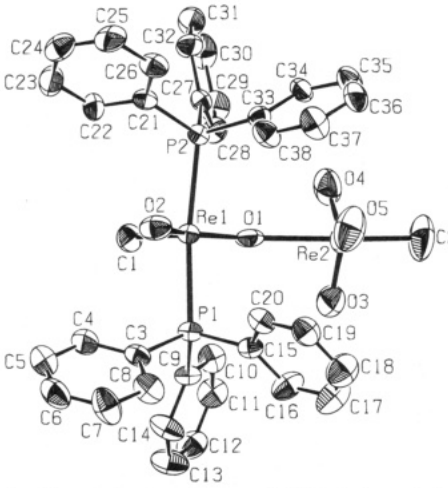

Figure 2. Crystal structure of bis(triphenylphosphine)-methyldioxorhenium(V)·MTO (**3a**) (PLATON) without hydrogen atoms. Thermal ellipsoids correspond to 50% equiprobability. Important distances (Å) and angles (deg): Re1—P1, 2.479 (2); Rel—P2, 2.486(2); Rel—O1, 1.754(8); Re1—O2, 1.715(7); Re1—C1, 2.11(1); Re2—O1, 2.377(7); Re2—O3, 1.686(9); Re2—C2, 2.03(1); P1—Rel—P2, 169.98(8); O1—Re1—P1, 89.1(2); O2—Re1—P1, 88.7(2); O1—Re1—O2, 148.0(4); C1—Re1—P1, 93.5(3); C1—Re1—O1, 105.1(4); C1—Re1—O2, 107.0(4); O1—Re2—O3, 84.7 (3); O1—Re2—C2, 178.2(6); O3—Re2—O4, 118.5(5); C2—Re2—O3, 96.2(6); Re1—O1—Re2, 162.2(4).

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Both phosphine ligands of the *tbp*-coordinated Re^{V} species are in *trans* positions to one another while the methyl and oxo groups occupy equatorial sites. The phosphine ligands are only slightly bent toward the oxo ligands (P1,Re,P2 169.98(8)°; P,Re,C1 mean 95.0(3)°; P,Re,O_{mean} 88.6(2)°). Triphenylphosphine ligands in *trans* positions are also observed in $ReIO_2(PPh_3)_2$.[10] By way of contrast, in octahedral d^2 complexes such as $[ReO_2{\cdot}py_4]^+$,[20] linear dioxometal structures (*trans*) are usual. The mean Re—P distance of 248.3(2) pm is as expected, *cf.* 248.8(3) pm for $ReIO_2(PPh_3)_2$.

Conclusion

Coordinative unsaturation and the presence of at least one oxo group appear to be the determining factors for rhenium complexes to act as catalysts in the olefination of aldehydes. The rhenium center should be in the oxidation state of +V in order to deoxygenate the aldehyde with reversible formation of Re(VII) species (*e.g.*, **3a** → CH_3ReO_3). Up to the present, the species $\{CH_3Re^{V}O_2\}$ and $\{Cl_3Re^{V}O\}$, stabilized by phosphines, fulfill these requirements but are certainly far away from being optimized catalysts of this useful CC-coupling reaction.

Experimental Section

All experiments were carried out under nitrogen using Schlenk techniques. The starting compounds **1**[2,3c] and bis(triphenylphosphine)trichlorooxorhenium (**4**)[11] were prepared according to literature methods. Triphenylphosphine was recrystallized from hexane before use. The other chemicals were used as purchased. ^1H NMR (400 MHz) spectra were recorded at JEOL JNM GX-400, mass spectra were recorded at 70 eV, Finnigan MAT 311-A. Elemental analyses were performed in the microanalytical laboratory of the authors' institute (M. Barth). Mass spectra (m/z values) are based on ^{187}Re isotope.

(1) Crystal Structure Determination. Single crystals suitable for X-ray analyses of compound **3a** were grown by standard techniques from diethyl ether solutions. Preliminary examination and data collection was carried out with Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer at 23 ± 1 °C. Final cell constants were obtained by least-squares refinement of 25 automatically centered high-angle reflections ($39.9° < 2\Theta < 43.8°$). Data were collected in ω-scan mode, orientation control reflections were monitored after every 200 reflections, and the intensities of three reflections were checked every 3600 s. An absorption correction was performed based on ψ scans (T_{max}/T_{min} **3a**: 99.9/91.52). No extinction correction was necessary for **3a**. Crystal data and intensity collection parameters are summarized together with details of the refinement in Table 3.

The structure was solved by Patterson methods and subsequent difference Fourier maps. Full-matrix least-squares refinement was carried out by minimizing $\Sigma w(|F_o| - |F_c|)^2$. Hydrogen atoms in **3a** were calculated in their ideal positions (d_{C-H} 96 pm), included in the data set, but were not refined. Scattering factors and anomalous dispersion corrections were taken from ref 21. The refinement converged at shift/err <0.001, and a final difference Fourier map showed no significant features. The refinement of the enantiomorphic structure model for **3a** resulted in higher *R* values ($R = 0.031$; $R_w = 0.036$). All calculations were performed on a DECstation 5000/25 computer with the programs SDP,[22] CRYSTALS,[23] and PLATON.[24] For further details of the crystal structure determination, the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche-technische Information mbH. D-76344 Eggenstein-Leopoldshafen (Germany) may be contacted, quoting the reference to this paper, the names of the authors, and the registration number CSD-58411.

Table 3. Summary of Crystal Data and Details of Intensity Collection for Bis(triphenylphosphine)-methyldioxorhenium(V)·MTO (3a)

Crystal Data	
formula	$C_{38}H_{36}O_5P_2Re_2$
formula weight, amu	1007.1
crystal system	monoclinic
space group	*Cc* (Int. Tab. No. 9)
crystal size, mm	0.38 × 0.20 × 0.18
crystal color and habit	red prism
a, pm	1393.5(4)
b, pm	1367.5(1)
c, pm	1928.0(5)
β, deg	102.67(1)
volume, $pm^3 \times 10^6$	3585
Z	4
density(calcd), g cm^{-3}	1.866
μ(Mo Kα), cm^{-1}	70
F_{000}	1936
Data Collection	
temperature, °C	23
monochromator	highly oriented graphite crystal
scan time, s	variable; max 90
scan width, deg	(1.3 + 0.30 tan θ)
2θ range, deg/octants	4.0–50.0/*h*,*k*,±*l*
background	±25% additional scans at each end of scan
reflections collected (independent)	5898 (3241)
R(merge)	0.014 (F_o)
observed reflections (NO)	3208 ($I > 1.0$)
Solution and Refinement	
system used	CRYSTALS
solution	heavy-atom methods
refinement method	full-matrix least-squares
weighting scheme	unit weights
number of parameters refined	424
final R/R_w indices (all data)[a]	0.023/0.025
data-to-parameter ratio	7.6:1
largest difference peak, e $Å^{-3}$	1.1
largest difference hole, e $Å^{-3}$	0.5
largest shift/err	<0.0001

[a] $R = \Sigma||F_o| - F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

(2) (η^2-Diphenylacetylene)methyldioxorhenium (2). To a solution of **3a** (250 mg, 0.25 mmol) in 10 mL of toluene was added 90 mg (0.5 mmol) of diphenylacetylene. The mixture was stirred at room temperature for 24 h. The initial brown colour turned slowly to yellow. The solution was then transferred to a chromatography column charged with silylated silica (Merck No. 7719, 70-230 mesh). Elution with ether/hexane (1:5) produced a yellow band. Evaporation of the solvent *in vacuo* yielded 160 mg (78% based on Re). IR (KBr): ν (cm^{-1}) 3054 w [ν(C=C—H)], 2928 w [ν(C—H)], 2923 w, 1442 m, 970 s [ν(Re=O)], 934 vs [ν(Re=O], 764 m, 689 s. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 2.64 (Me, s, 3H), 7.45–7.85 (C_6H_5, m, 10H). CI-MS: *m/z* 413 ([$M^+ + H^+$], rel int 100) 397 ([$M^+ - CH_3$], 4), 178 ([PhC≡CPh], 48).

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Anal. Found (calcd for $C_{15}H_{13}O_2Re$, 411.47): C, 43.66 (43.79); H, 3.27 (3.18); O, 7.7 (7.78); Re, 46.0 (45.27).

(3) Bis(triphenylphosphine)methyldioxorhenium(V)·MTO (3a). PPh_3 (520 mg, 2 mmol) was added to a solution of 250 mg (1 mmol) of MTO in ether (10 mL). The mixture was stirred at room temperature for 24 h. The initial yellow color changed to red and brown. After 30 min a orange solid started to precipitate. After 24 h the solution was filtered, and the remaining orange powder was washed two times with 10 mL of ether. Yield: 350 mg (70%). Mp: 125 °C. IR (KBr): ν (cm^{-1}) = 3049 w [ν(C=C–H)], 1434 s, 1098 s, 934 s [ν(Re=O)], 927 s [ν(Re=O)], 810 vs, 747 s, 692 s. ^1H NMR (400 MHz, $CDCl_3$, −55 °C): δ (ppm) 1.81 (Re(VII)–Me, s, 3H), 3.02(Re(V)–Me, s, 3H), 7.44–7.61 (C_6H_5, m, 30H). ^{31}P NMR (160.8 MHz, $CDCl_3$, −55 °C): δ (ppm) 9.9 (s). FAB-MS: *m/z* 758 ($[M]^+$ − MTO, rel int 2), 279 ($[O{=}PPh_3]^+$, 75), 262 ($[PPh_3]^+$, 100), 250 ($[MTO]^+$, 8). Anal. Found (calcd for $C_{38}H_{36}P_2O_5Re_2 \cdot 0.5(C_2H_5)_2O$, 1007.06): C, 46.01 (46.01); H, 3.86 (3.95); P, 6.18 (5.93) Re, 36.13 (35.66).

(4) Bis(tricyclohexylphosphine)methyldioxorhenium(V)·MTO (3b). Pcy_3 (560 mg, 2 mmol) was added to a solution of 250 mg (1 mmol) of MTO in ether (10 mL). The mixture was stirred at room temperature for 24 h. The color turned immediately to deep-red. After a few minutes a red solid started to precipitate. After 3 h the solution was filtered, and the remaining red powder was washed two times with 10 mL of ether. Yield: 340 mg (65%). IR (KBr): ν (cm^{-1}) 2928 vs [ν(C–H)], 2850 s, 1445 m, 927 s [ν(Re=O)], 809 s. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 1.1–2.25 (m). ^{31}P NMR (160.8 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.4 (s). FAB-MS: *m/z* 794 ($[M]^+$ − MTO, rel int 7), 514 ($[MeReO_2Pcy_3]^+$, 41), 297 ($[O{=}Pcy_3]^+$, 35), 281 ($[Pcy_3]^+$, 100), 250 ($[MTO]^+$, 8). Anal. Found (calcd for $C_{38}H_{72}P_2O_5Re_2$, 1043.34): C, 43.48 (43.74); H, 6.91 (6.95); P, 6.04 (5.94); Re, 35.97 (35.69).

(5) Olefination of Aldehydes. (a) Stoichiometric Reaction of 4-Nitrobenzaldehyde, Ethyl Diazoacetate, and 3a. After the mixture of 4-nitroaldehyde (76 mg, 0.5 mmol), ethyl diazoacetate (0.07 mL, 0.7 mmol), and **3a** (503 mg, 0.5 mmol) in THF (5 mL) was stirred at room temperature for 2 h, the solvent was removed under vacuum, and the brown residue was extracted with diethyl ether. The GC–MS analysis of the concentrated extract showed that the olefin $4\text{-}O_2NC_6H_4CH{=}CHCOOEt$ (*E*/*Z* mixture, 46/54) was formed without any ether-soluble side products.

(b) Catalytic Reaction of 4-Nitrobenzaldehyde, Ethyl Diazoacetate, PPh_3, and 5 mol % of 3a. Ethyl diazoacetate (0.14 mL, 1.4 mmol) was added to the orange solution of 4-nitrobenzaldehyde (151 mg, 1.0 mmol), PPh_3 (262 mg, 1 mmol), and **3a** (50 mg, 0.05 mmol) in THF (6 mL). Gas (N_2) evolved, and the solution turned brown. After being stirred at 25 °C for 2 h, the mixture was concentrated under vacuum and the residue was chromatographed on silica gel with *n*-hexane/ethyl acetate (8:1 to 6:1) as eluent. Yellow crystals were isolated from the concentrated yellow eluent as a *E*/*Z* mixture (78/22) of $4\text{-}O_2NC_6H_4CH{=}CHCOOEt$ (196 mg, 89%).

(c) Catalytic Reaction of 4-Nitrobenzaldehyde, Ethyl Diazoacetate, PPh_3, and 5 mol % of 4 (1 mol %). Ethyl diazoacetate (0.6 mL, 6 mmol) was added to the yellow suspension of 4-nitrobenzaldehyde (736 mg, 4.87 mmol), PPh_3 (1.3 g, 5 mmol), and **4** (200 mg, 0.24 mmol) in THF (30 mL) at 10 °C. Gas (N_2) evolved quickly, and the solution turned brown. The same amount of organic educts were added every 1.5 h. After the total amount of 3.68 g (24.37 mmol) of 4-nitrobenzaldehyde, 3.0 mL (30 mmol) of ethyl diazoacetate, and 6.50 (25 mmol) of PPh_3 were added, the catalyst was still active. The mixture was stirred for another 6 h at 25 °C. The solvent was removed *in vacuo*, and the residue was chromatographed on silica gel with *n*-hexane/ethyl acetate (8:1 to 6:1) as eluent. Yellow crystals were isolated from concentrated yellow eluent as a *E*/*Z* mixture (96/4) of $4\text{-}O_2NC_6H_4CH{=}CHCOOEt$ (4.86 g, 90%). The TON based on rhenium is >90.

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Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles for **3a** (9 pages). Ordering information is given on any current mashead page.

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