191. Insertion Reactions of $[ReH(CO)_{5-n}(PMe_3)_n]$ Complexes ($n = 2$–4) with Aldehydes, CO_2, and Activated Acetylenes

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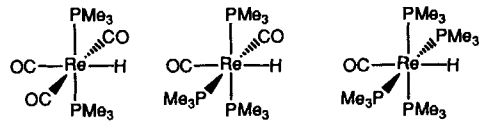
The complexes of the type $[ReH(CO)_{5-n}(PMe_3)_n]$ ($n = 2$, **1**; $n = 3$, **2**; $n = 4$, **3**) were reacted with aldehydes, CO_2, and RC≡CCOOMe (R = H, Me) to establish a phosphine-substitutional effect on the reactivity of the Re–H bond. In the series **1**–**3**, benzaldehyde showed conversion with only **3** to afford a (benzyloxy)carbonyltetrakis(trimethylphosphine)rhenium complex **4**. Pyridine-2-carbaldehyde allowed reaction with all hydrides **1**–**3**. With **1** and **2**, the same dicarbonyl[(pyridin-2-yl)methoxy-*O*,*N*]bis(trimethylphosphine)rhenium **5b** was formed with the intermediacy of a [(pyridin-2-yl)methoxy-*O*]-ligated species and extrusion of CO or PMe_3, respectively. The analogous conversion of **3** afforded the carbonyl[(pyridin-2-yl)methoxy-*O*,*N*]tris(trimethylphosphine)rhenium(*I*) **7b**. While **1** did not react with CO_2, **2** and **3** yielded under relatively mild conditions the formato-ligated $[Re(HCO_2)(CO)(L)(PMe_3)_3]$ species (**8** (L = CO) and **9** (L = PMe_3)). Methyl propiolate and methyl butynoate were transformed, in the presence of **1**, to $[Re\{C(CO_2Me)=CHR\}(CO)_3(PMe_3)_2]$ systems (**10a** (R = H), and **10b** (R = Me)), with prevailing α-metallation and *trans*-insertion stereochemistry. Similarly, $HC{\equiv}CCO_2Me$ afforded with **2** and **3**, the α-metallation products $[Re\{C(CO_2Me)=CH_2\}(CO)(L)(PMe_3)_3]$ **11** (L = CO) and **12** (L = PMe_3). The methyl butyonate insertion into **2** resulted in formation of a mixture of the (*Z*)- and (*E*)-isomers of $[Re\{C(CO_2Me)=CHMe\}(CO)_2(PMe_3)_3]$ (**13a, b**). In the case of the conversion of **3** with $MeC{\equiv}CCO_2Me$, a Re–H *cis*-addition product $[Re\{(E)\text{-}C(CO_2Me)=CHMe\}(CO)(PMe_3)_4]$ (**14**) was selectively obtained. Complex **11** was characterized by an X-ray crystal-structure analysis.

Based on *Pauling*'s electronegativity arguments [1], *Labinger* and *Bercaw* [2] proposed that the strength of L_nM–H bonds (M = transition metal) is expected to decrease with decreasing electronegativity of the metal center. This would then also lead to increasing hydridicity of the H ligand. Therefore, it is assumed that reaction steps which require initial bond cleavage like insertion reactions are accelerated, when weak L_nM–H bonds are present. In addition, lower kinetic barriers might be expected for the transfer of hydrides from complexes with a strong $L_nM^{\delta+}$–$H^{\delta-}$ polarization to polar substrates. Through measurements of deuterium quadrupole relaxation times [3], a quite polar character of the Re–H bond was established for $[ReH(CO)_{5-n}(PMe_3)_n]$ compounds. However, the measurements were too insensitive to conclude a significant change in the Re–H bond polarity with increasing *n*. From investigations of protonations of $[ReH(CO)_{5-n}(PMe_3)_n]$ complexes, which led to subsequent (H_2) complex formations [4], the hydridicities increasing in the order $n = 4 > 3 > 2$ seemed to be established.

To further support the idea that phosphine substitution can enforce the hydridic polarization of the Re–H bond and hence enhance the propensity to undergo insertion processes, we set out to investigate the reactivity of $[ReH(CO)_{5-n}(PMe_3)_n]$ complexes (n = 2–4) toward two types of aldehydes, CO_2, and activated acetylenes.

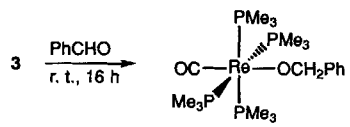
Results and Discussion. – For a systematic study of the insertion reactions, the species **1**–**3** were selected as starting materials. These compounds represent a series of specific



1 2 3

stereoisomers which display hydride/PMe_3 *cis*- and hydride/CO *trans*-configurations. The syntheses of **2** and **3** were recently reported [5], and **1** was obtained in high yield by reduction of $[ReCl(CO)_3(PMe_3)_2]$ with Na in THF and subsequent acidification with H_2O.

Out of the series of compounds **1–3**, only **3** reacted with benzaldehyde in toluene to yield a benzyloxy complex **4** (*Eqn. 1*) which was isolated as pale yellow O_2-sensitive crystals in 89% yield. Note, that alkoxide complexes of the type $[Re(OR)(CO)_3L_2]$ were prepared earlier by *Bergman* and *Simpson* [6] by non-insertive reaction paths.

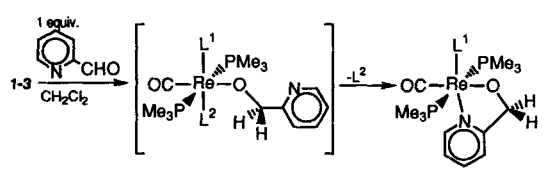


(1)

4

The ^{1}H-NMR spectrum of **4** shows, among other resonances, a characteristic *s* at 4.59 ppm, and the $^{13}C\{^1H\}$-NMR spectrum reveals a *quint.* at 76.7 ppm. Both absorptions correspond to ^{1}H or ^{13}C signals of the CH_2 group, which are shifted to lower field with respect to those of free benzyl alcohol ($\Delta\delta(^1H) = 0.06$ ppm, $\Delta\delta(^{13}C) = 11.3$ ppm). From the *quint.* coupling pattern of the CH_2 and the CO resonances and a *s* in the ^{31}P-NMR spectrum, the 'equatorial' arrangement of the P-substituents in **4** is deduced.

Since benzaldehyde did not react with the bis- or tris(trimethylphosphine)-substituted complexes **1** and **2**, we sought to apply a more activated (electrophilic) aldehyde, like pyridine-2-carbaldehyde, to achieve reactions with all derivatives **1–3** (*Eqn. 2*). However, the expected primary insertion products **5a**, **6a**, and **7a**, respectively, underwent further fast subsequent replacement of a *cis*-ligand at room temperature. The (pyridin-2-yl)methoxide ligand preferably acts as an *N,O*-chelating moiety, which quite often induces elimination of *cis* ligands [6]. In addition, this process is promoted by the *cis*-labilizing effect of the newly formed alkoxide group. The ligand replacements from **5a** and **6a** yielded the same product **5b** (*Eqn. 2*) since in the case of **5a**, a CO, and in the case of **6a**, a PMe_3 group was expelled. Complex **7a** was transformed to **7b** with extrusion of a PMe_3 moiety. The preparative conversions of **1** and **2** to **5b** were conducted at 0°, while the



(2)

−20°C	**5a** $L^1 = L^2 = CO$	−20°C	**5b** $L^1 = CO$
−20°C	**6a** $L^1 = PMe_3$, $L^2 = CO$	r. t.	**6b** $L^1 = CO$
−60°C	**7a** $L^1 = L^2 = PMe_3$	0°C	**7b** $L^1 = PMe_3$

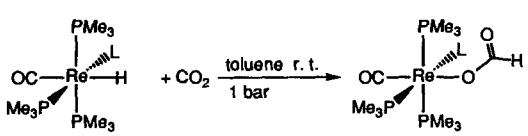
reaction of **3** leading to **7b** was performed between −60° and room temperature. The chelate complexes **5b** and **7b** were isolated in good yields and characterized by IR and NMR spectroscopy, and MS as well as by elemental analyses.

A detailed NMR study of the reaction of **1–3** with pyridine-2-carbaldehyde revealed that in the case of **1**, **5a** was not detectable at temperatures of −20° or higher. However, since the formation of **6a** and **5b** from **2** required different initiating temperatures (−20° and room temperature, resp.), **6a** could be identified by ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy at −20°. Similarily, for the conversions of **3** to **7a** and **7a** to **7b**, an approximate difference of 60° was found for their initial temperature so that **7a** could again be characterized by NMR techniques at low temperature.

The ^{1}H-NMR spectra of the alkoxy derivatives **6a** and **7a** show a *s* at 4.78 and 4.60 ppm, respectively, which is attributed to the methylene protons. In the ^{13}C-NMR spectrum, the CH_2 resonance of **6a** appears as a *d* (^3J(P,C) = 9 Hz), apparently due to the coupling with just the P-nucleus *trans* to the CO group. The CH_2 group of **7a** gives rise to a *quint.* (^3J(P,C) = 4 Hz). The ^{1}H- and ^{13}C-NMR resonances of the pyridinyl rings in **6a** and **7a** can all be identified. The CO signals are detected as a br. *s* for **6a** and as a *quint.* for **7a**. The ^{31}P-NMR spectrum of **6a** shows a *d* and a *t* with the intensity ratio of 2:1, indicative of the *mer*-tris(trimethylphosphine) arrangement, and the spectrum of **7a** displays a *s* for the four chemically equivalent P-nuclei.

In the IR spectra, **5b** shows two $\tilde{\nu}$(CO) bands consistent with the presence of two *cis*-CO groups. Complex **7b** exhibits one $\tilde{\nu}$(CO) absoption at a very low wave number (1783 cm^{-1}), which is in accord with a residual ligand environment of merely donor substituents. The ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra confirm the C_s symmetrical structures of **5b** and **7b**. The chelation of the (pyridin-2-yl)methoxide moiety is indicated by the resonances of the methylene protons [7], which are shifted *ca.* 0.5–0.6 ppm low field in **5b** and **7b** compared to **6a** and **7a**. The ^{13}C-NMR spectra of **5b** and **7b** reveal two broad CO signals for **5b** and a P-coupled CO *t* resonance for **7b**. The ^{1}H- and ^{13}C-NMR spectroscopic data of the chelate rings of **5b** and **7b** are not conclusive with respect to the O/N orientation of this group. A NOE experiment on **7b** does not provide further information for its structural assignment, *i.e.*, irradiation of the *H*–*C*(6) resonance at 8.92 ppm does not effect a noticeable polarization transfer to the *C*O signal at 201.8 ppm. Based on the comparable δ of the *C*O absorption of **4**, **6a**, **7a**, and **5b** and **7b**, a O-donor/CO *trans*-arrangement seems to be reasonable. Also an orientation with the N-donor *trans* to the CO ligands is expected to cause a low-field shifts of the CO signal [7]. An attempt to induce isomerization of the O/N chelate by heating **7b** to 80° for 5 days in toluene solution was unsuccessful; **7b** remained stable under these conditions. The ^{31}P-NMR spectrum of **5b** reveals a *s* resonance, and that of the *mer*-PMe_3 complex **7b** a *d* and a *t*, like in **6a**.

The exploration of the reactivity of **1–3** was then continued with investigations on insertion reactions of CO_2 [8] [9]. Complex **1** was found to be inert towards CO_2 (1 bar) in toluene or in polar solvents, like MeCN or DMF, from room temperature up to 80°. Complexes **2** and **3** reacted with CO_2 (1 bar) in toluene at room temperature (reaction times *ca.* 1.5 h for **2** and a few s for **3**) according to *Eqn. 3*, yielding the formato-*O* complexes **8** (orange) and **9** (colorless), respectively, both in high yield (98%). *Allen* and *Green* [10] studied the reaction of *cis*-[ReH(CO)(PMe_3)$_4$] with CO_2 and obtained a product which is spectroscopically identical to **9**. However, the insertion into *cis*-[ReH(CO)(PMe_3)$_4$] required more rigorous reaction conditions (3 bar CO_2, 70°), and at room temperature no reaction took place.



2, 3

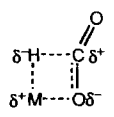
8 L = CO
9 L = PMe_3

(3)

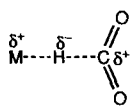
The IR spectrum of **8** shows two intense $\tilde{\nu}$(CO) bands in agreement with the presence of two *cis*-arranged CO groups. In addition, a characteristic $\tilde{\nu}$(CH,formato) and a $\tilde{\nu}(CO_2)$ absorption are identified. The ^{1}H-NMR spectrum of **8** displays, among others, a characteristic resonance at 8.42 ppm (^4J(P,H) = 1.3 Hz) which is assigned to *H*–COO. In the ^{1}H-coupled ^{13}C-NMR spectrum, one finds a *d* at 167.5 ppm (^1J(C,H) = 194 Hz) which has a similar chemical shift as the C-atom of formic acid (166.4 ppm) and a comparable ^1J(C,H) coupling as the formate anion (194.8 Hz). These data confirm the presence of the HCOO moiety. The other ^{1}H-, ^{13}C-, and the ^{31}P-NMR data of **8** are close to those of **2**, which suggests that the carbonyl/phosphine ligands of **2** and **8** have an identical configuration.

It should be noted that the insertion reaction of **2** with CO_2 can be accelerated in a polar solvent; *e.g.*, in DMF, the reaction was completed within 20 min. This observation is in agreement with those made for the CO_2 reaction of [ReH(bipy)(CO)$_3$] (bipy = 2,2′-bipyridine) [11] and suggests a polar character of the transition state for such processes. The reaction of **2** according to *Eqn. 3* was not influenced by the presence of PMe_3, which rules out a dissociative mechanism proceeding with loss of PMe_3. When **8** was heated to 100° for 3 days, no decarboxylation, *i.e.*, reversal of *Eqn. 3* was noticed. In contrast to this, **9** lost CO_2 upon heating in toluene at 100° for 2 d. The latter process was accompanied by a ligand-sphere rearrangement, and *cis*-ReH(CO)(PMe$_3$)$_4$] was formed; no **3** was detected under these conditions.

As mentioned above, insertions of CO_2 are thought to require a rather polar $M^{\delta+}$–$H^{\delta-}$ bond and were suggested to pass through polar transition states **A** or **B** [11]. *Darensbourg* and *Ash* [12] indeed found a correlation between the rates of insertion of CO_2 into $[MH(CO)_4L]^-$ complexes (M = Cr, Mo, W; L = CO, PR_3) and the nucleophilicity of these species, which depends on the donating ability of the ligand L. Apparently, the tri- and tetraphosphine-substituted complexes **2** and **3** have attained sufficient nucleophilicity for reactions with CO_2, while the diphosphine-substituted compound **1** has not. It is noteworthy that the observation that the reaction to **8** could in contrast to **9**, not be reversed, even not at a temperature of 100°, may imply weaker Re–H bonds in **8** than in **9**.

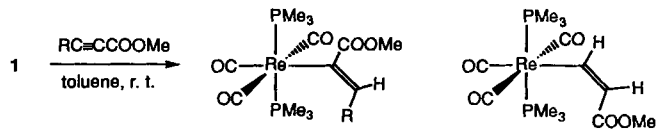


A



B

In addition to the reactions of (C=O)-containing substrates with complexes **1**–**3**, their insertion chemistry with activated acetylenes RC≡CCOOMe (R = H, Me) were studied. In the presence of methyl propiolate or methyl but-2-ynoate, **1** was converted, in toluene solution, to the olefin derivatives **10a**, **b** (*Eqn. 4*) in 90 and 84% yield, respectively. Their formations at room temperature required quite different reaction times: a few s for **10a** and 14 d for **10b**. An ^{1}H-NMR spectroscopic inspection of the reaction to **10a** revealed that, in addition to this α-metalation compound, a minor amount of the β-metalation isomer **10c** was formed in *ca.* 5% yield; the latter could not be isolated from the reaction mixture and its structure was solely derived from the ^{1}H-NMR data. The double-bond configuration of **10c** revealed, in addition to β-metalation, Re–H *trans*-addition across the acetylenic triple bond. Products **10a** and **10b** were formed by α-metalation and *trans*-addition.



10a R = H
b R = Me

10c

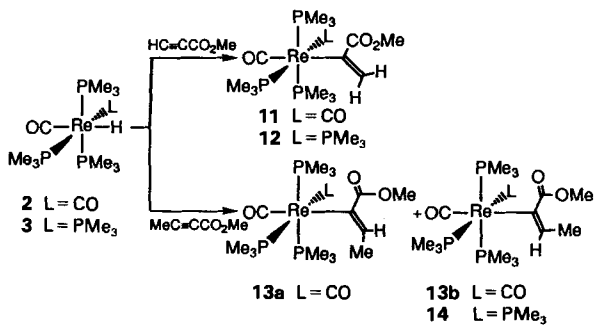
(4)

The ^{1}H-NMR of **10c** shows two *d*/*t* at 8.88 and 7.39 ppm with J(P,H) of 4.6 and 3.4 Hz, respectively. Based on their quite low-field position these resonances are assigned to H–C(α) and H–C(β) of the C(β)-metal connected acrylate unit. The vicinal ^3J(H,H) value of 14.8 Hz is consistent with the *cis*-position of these protons [13]. In the ^{1}H-NMR spectrum of **10a**, a geminal ^2J(H,H) coupling of 4.5 Hz of the two methylene protons is recognized, and **10b** shows a typical signal for an olefinic H–C(β). The NMR data of **10a** and **10b** resemble closely those of the [Re{C(CO_2Me)=CHR}($CO)_2$($PMe_3)_3$] complexes (*vide infra*), where the derivative with R=H was characterized by an X-ray structure determination.

In an ^{1}H-NMR experiment, the complex [ReD($CO)_3$($PMe_3)_2$] (D-**1**) was reacted with HC≡CCO_2Me in (D_8)toluene. The ^{1}H-NMR spectra of the product [Re{C(COOMe)=CHD}($CO)_3$($PMe_3)_2$] (D-**10a**) show no signal for a H-atom *trans* to the Re-atom (at 6.65 ppm in **10a**), indicating that *trans*-insertion had occurred.

From the temperature-dependent ^{13}C-NMR spectra of **10b** in C_6D_6, it was derived that the olefinic group shows hindered rotation around the Re–C bond. At room temperature, 3 signals for the CO groups are observed. Two of them are assigned to chemically inequivalent *cis* CO groups. Their inequivalence is explained in terms of an asymmetric environment induced by the preferred in-plane (in-plane with the Re($CO)_3$ unit) conformation of the methacrylic moiety. At 80°, these two signals collaps to one signal indicating now free rotation of the olefinic group on the NMR time scale.

Complexes **2** and **3** were also reacted with HC≡CCO_2Me or MeC≡CCO_2Me. Exclusively α-metalations were observed with Re–H *cis*-(**14**, **13b**) and *trans*-additions (**11**, **12**, and **13a**; *Eqn. 5*), and the reactions proceeded at room temperature with high overall



(5)

yields. The isomeric complexes **13a** and **13b** were characterized as a 3:7 mixture which could not be separated by crystallization or chromatography. The **13a**/**13b** ratio changed only marginally with the reaction temperature, a 27:73 ratio being obtained at −10°. The structures of complexes **11**–**14** were determined by IR, MS, and NMR spectroscopy, and in addition to this, **11** was characterized by a single-crystal X-ray diffraction study. [ReD($CO)_2$($PMe_3)_3$] (D-**2**) and [ReD(CO)($PMe_3)_4$] (D-**3**) reacted with HC≡CCOOMe in (D_8)toluene to afford the (*E*)-configurated products (D- and Re-

atom *trans*), confirming the *trans*-insertion for these processes. A [W{(*Z*)-C(COOMe)=C(Ph)H}$(CO)_2(NO)(PMe_3)_2$] complex [13] configurationally related to **13a** underwent irreversible thermal (*Z*/*E*)-isomerization. In analogy to this, **13a** is suggested to be the kinetic product, since it also faces considerable repulsion between the *cis*-arranged Re fragment and the Me group. However, an attempt to isomerize **13a** into the (*E*)-compound **13b** by heating it in toluene for 4 d at 100° failed.

The ^{1}H-NMR spectra of **11** and **12** exhibit resonances for the types of olefinic protons at 6.48 and 6.47 ppm and 5.3 and 5.49 which are geminally coupled with ^2J(H,H) values of 4.8 and 5.6 Hz, respectively. The low-field resonances are assigned to the H-atoms *trans* to the Re-atom (H_{trans}) [13]. These show generally a stronger ^4J(P,H) coupling than the H_{cis} nuclei [13]. ^4J(P,H) Coupling of the *trans*-positioned (in the octahedron) ^{31}P nuclei is occurring to both CH_2 protons of **11**, while the ^{31}P atom *trans* to CO couples only with H_{trans}. Complex **12** has remarkably small ^4J(P,H) couplings to the olefinic protons (1.0 and 1.6 Hz), a phenomenon which is yet unexplained. The ^{13}C-NMR spectra of **11**–**14** consist among others of C(olef.) signals in the range of 151–164 and 124–138 ppm which are attributed to the C(α) and C(β) atoms, respectively.

The assignment of the double-bond configuration of **14** is based on the relative high-field chemical shift of the ^{1}H-NMR resonance typical of H_{cis} nuclei (5.64 ppm). A H_{trans} signal would be expected to appear in the range 6–7.5 ppm (*cf.* also the ^{1}H-NMR spectra of **10a**, **10b**, **11**, **12**, **13a**, and **13b**). Further support for structure **14** is provided by the ^3J(C,H) coupling of 16.3 Hz between *H*–C(β) and the *C*OOMe which falls into the expected range for such *trans*-positioned groups at the double bond [14].

The reaction of **3** with MeC≡CCOOMe was complete within 1 h at room temperature. By low-temperature ^{1}H-NMR spectroscopy at −20°, it was checked further, whether the formation of **14** passes through an intermediate not detectable at room temperature. However, no further signals except those of **14** could be recognized in the low-temperature experiment. The reason for the exclusive formation of the *cis*-addition product **14** may have to do with the substantial steric hindrance exerted by the $Re(CO)(PMe_3)_4$ fragment which is largest compared to the other ReL_5 fragments of the series **1**–**3.** The *trans*-addition mode of the methyl butynoate molecule is sterically more demanding than the *cis* one. Finally, it should be mentioned that *cis*-[$ReH(CO)(PMe_3)_4$] did not react with MeC≡CCOOMe under conditions comparable to those of the analogous transformation of **3**. The observation that **3** has a higher reactivity in comparison to *cis*-[$ReH(CO)(PMe_3)_4$] may be related to the larger *trans*-influence of the CO ligand with respect to the PMe_3 group. For this reason, complexes **1**–**3** were all of H/CO *trans*-configuration, thus preventing interference of a superimposed CO *trans*-influence on this analysis.

Conclusions. – Summarizing the effects of *cis*-phosphine substitution in [$ReH(CO)_{5-n}(PMe_3)_n$] complexes with respect to their capability to undergo insertion reactions with RCHO (R=Ph, py) and CO_2, one can clearly see that the reactivity is enhanced with an increasing number of phosphine substituents. This demonstrates that electronic factors are dominating since on pure steric grounds, an inverse dependence on *n* and hence a reactivity order **3** < **2** < **1** would be expected. It will remain an open question whether the correlation between the reactivity and the number *n* of the PMe_3 substituents is determined by the kinetics of these reactions, *i.e.*, formation of appropriate transition states due to the increase of the $Re^{\delta+}$–$H^{\delta-}$ bond polarity, or is based on the thermodynamics of the reactions, *i.e.*, weakening of the Re–H bond.

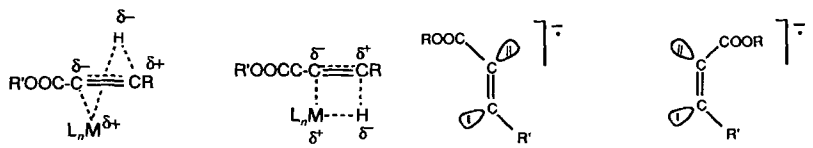
A comparison of the conditions of the investigated acetylene insertion of **1**–**3** shows that the HC≡CCO_2Me insertions are in any case quite fast and do at room temperature not distinguish between the type of metal fragment (*Table 1*). For the MeC≡CCO_2Me

insertions there is, however, a noticable discrimination in the reaction rates of **1**, **2**, and **3**. The observed qualitative order of rates is: $k(\mathbf{1}) < k(\mathbf{2}) < k(\mathbf{3})$. This is in contrast with the expectation that the larger steric demand of the corresponding ReL_5 fragment would lead to lower rates. However, this would again cope with the electronic properties of these complexes, *i.e.*, increased electron richness of the metal center (increased hydridic polarization of the Re–H bond) gives rise to lower kinetic barriers. The reaction mechanisms for the insertions of such activated acetylene insertions are not definitely known. There are, however, two anticipated pathways along which these reactions might proceed [15].

Table 1. *Acetylene Insertions of* **1–3**

Starting material	$RC{\equiv}CCO_2Me$	Product	Reaction time at r.t.
1	R=H	**10a, 10c**	s
2	R=H	**11**	s
3	R=H	**13a, 13b**	s
1	R=Me	**10b**	14 d
2	R=Me	**12**	7 h
3	R=Me	**14**	1 h

One mechanistic alternative of the acetylene insertions involves *antara* or *supra* transition states **C** and **D**, leading to *cis*- or *trans*-addition products, respectively. These models can explain the observed regiospecificity of the insertions with the given polarization of the reacting partners $L_nM^{\delta+}-H^{\delta-}$ and $R'C^{\delta+}{\equiv}C^{\delta-}-COOR$. The preference for *antara vs. supra* geometries can, however, not be rationalized on the basis of this model.



Another reaction sequence for a $R'C{\equiv}CCOOR$ insertion was suggested by *Clark et al.* [16]. For *trans*-$[PtH_2(PR_3)_2]$ compounds, a cage-trapped radical pathway with an initial single-electron transfer was claimed and may be applied to the reactions of **1–3** as well.

$$[MHL_n] + R'C{\equiv}CCOOR \rightarrow [MHL_n^{+\cdot}, R'C{\equiv}CCOOR^{-\cdot}]$$

$$H^+ + [ML_n]^{\cdot} \leftarrow [MHL_n]^{+\cdot} \rightarrow [ML_n]^+ + H^{\cdot}$$

The character of the $[MHL_n]^{+\cdot}$ species representing an $H^{\cdot}$ or an H^+ transfer agent (hydridic parent hydrides should lead to an $H^{\cdot}$, less hydridic hydrides to an H^+ source) determines the regiochemistry of the addition, since $H^{\cdot}$ or H^+ will combine with the radical or the anionic centers of the acetylene radical anion. They may be arranged in a *trans*- or *cis*-fashion of the R'- or COOR-substituted C-atoms, respectively (see **E** and **F**). This would also explain the preference for a *trans*- or *cis*-addition mode. Assuming such a mechanism, **10a**, **10b**, and **11–14** are formed with α-metalation from an $H^{\cdot}$ source, except for the generation of **10c** which requires an H^+ donator. The latter observation may be interpreted in terms of a reduced hydridic character of **1** causing an ambiphilic

character of the $[MHL_n]^+$ species. A higher propensity to form H^+ from $[MHL_n]^{+\cdot}$ may be anticipated for all higher CO-substituted hydride compounds. In this context, it should be mentioned that $[ReH(CO)_5]$ and $[MnH(CO)_5]$ [17], $[ReH(cp)_2]$ [14], $[OsH(C_6H_6)\{P(i\text{-}Pr)_3\}_2]^+$ [18], and $[RuClH(CO)(PPh_3)_3$(3,5-dimethyl-1*H*-pyrazole)] [19] are supposedly all H^+ sources as radical cations and less hydridic metal hydrides in their parent states, since they all generate β-metallation products upon addition of activated alk-1-ynes like HC≡CCOOMe, HC≡CCF$_3$, and HC≡CCN.

Crystal-Structure Determination of 11[1]). – A suitable crystal of **11** was grown from a saturated solution in hexane at 0°. For crystallographic and refinement data of **11**, see *Table 2*. From the *Figure*, it can be seen that the Re-atom in **11** has a pseudooctahedral

Table 2. *Crystal, Structure-Solution, and Refinement Data of* **11**

Empirical formula	$C_{15}H_{32}O_4P_3Re$	Temperature [K]	253
Color; habit	Colorless prism	Monochromator	highly oriented graphite crystal
Crystal size [mm]	0.3 × 0.3 × 0.4	2θ Range	4.0–52°
Space group	$P2_12_12_1$	Scan type	ω
a [Å]	9.037(3)	Scan speed	variable; 1.50 to 14.65°/min in ω
b [Å]	15.274(5)	Scan range (ω)	0.70°
c [Å]	16.508(9)	Independent reflections	1705 (R_{int} = 0.00%)
Volume [Å^3]	2279(2)	Observed reflections	1518 ($F > 6\sigma(F)$)
Z	4	Absorption correction	none
Formula weight	555.5	R_F	2.94
Density (calc.)	1.619 Mg/m^3	R_{F2}	3.44
Absorption coefficient	5.625 mm^{-1}	Goodness of fit	2.89
F(000)	1096	Weighting scheme	unit weights
Solution	Direct methods	Final maximum shift (esd)	0.002 (0.000)
Diffractometer used	*Siemens R3 m/V*	Max./min. residual electron	0.81/ – 0.81
Radiation	MoK_α (λ = 0.71073 Å)	Density [eA^{-3}]	

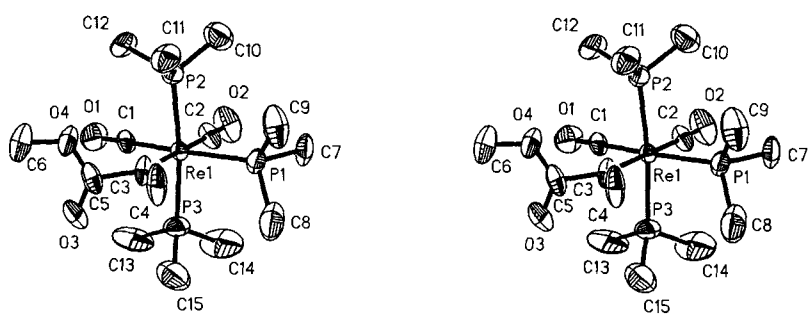


Figure. *Stereoview ORTEP plot of* **11**. Thermal ellipsoids drawn with 50% probability. Selected bond lengths and angles: Re(1)–P(1) 2.478(4), Re(1)–P(2) 2.403(5), Re(1)–P(3) 2.403(6), Re(1)–C(1) 1.890(13), Re(1)–C(2) 1.891(18), Re(1)–C(3) 2.154(18), C(1)–O(1) 1.182(18), C(2)–O(2) 1.172(24), C(3)–C(4) 1.393(30), and C(3)–C(5) 1.502(19) Å. P(1)–Re–P(2) 92.8(2), P(1)–Re(1)–P(3) 93.0(2), P(2)–Re(1)–P(3) 173.3(2), C(1)–Re(1)–C(3) 93.1(6), C(1)–Re(1)–C(2) 87.0(7), P(1)–Re(1)–C(3) 91.0(5), Re(1)–C(3)–C(4) 134.4(11), and Re(1)–C(3)–C(5) 116.3(13)°.

[1]) Crystal structure basis and solution were deposited at the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, England.

coordination geometry with only minor deviations from the ideal ligand arrangement. The bond lenghts of the Re–ligand distances fall into the range determined for other low oxidation state Re complexes [20].

The olefin moiety presumably acts as a π acceptor toward the Re-center, since its π system is oriented in the (Re1, P2, P3, C2) plane, which provides better π donation than the (Re1, P1, C1, C2) plane of the metal fragment. Maybe for steric reasons, the ester group is out-of-plane with the olefin system disregarding the possibility of energetically favorable π overlap.

We thank the *Swiss National Science Foundation* for financial support.

Experimental Part

General. All preparations and manipulations were carried out under dry N_2 by conventional *Schlenk* techniques. Solvents were dried and freshly distilled before use. Acetylene compounds were purchased from commercial suppliers. $[ReCl(CO)_3(PMe_3)_2]$ [21] and $[Re(CO)(PMe_3)_3L]$ (L = CO, PMe_3) complexes [3] were prepared according to published procedures. Column chromatography: silica gel *60* (*Merck*). Filtrations: *Lichroprep* (*Merck*) silica gel. IR Spectra: *Biorad-FTS-45* instrument. NMR Spectra: *Gemini-300-BB* instrument; ^1H at 300.08 MHz, ^{13}C at 75.46 MHz, and ^{31}P at 121.47 MHz; if not indicated otherwise, at r.t. δ(H) and δ(C) rel. to $SiMe_4$ and δ(P) rel. to H_3PO_4. Mass spectra: *Finnigan-MAT-8230* spectrometer; FAB spectra in 3-nitrobenzyl alcohol matrix.

[OC-6-12]-Tricarbonylhydridobis(trimethylphosphine)rhenium(I) ($[ReH(CO)_3(PMe_3)_2]$; **1**). $[ReCl(CO)_3(PMe_3)_2]$ (1 g, 2.18 mmol) was dissolved in THF (100 ml), and small pieces of Na (0.4 g, 17.4 mmol) were added at r.t. (reaction times 8–40 h; IR monitoring). After completion, the yellow soln. was filtered through *Celite* and cooled to 0°, and H_2O (43 µl, 2.4 mmol) was added. After warming to r.t., the solvent was evaporated and the residue extracted with hexane. After filtration over *Celite*, most of the solvent was evaporated and the remaining soln. left for crystallization at −30°: 0.83 g (90%). IR (hexane): 1919 (CO). ^1H-NMR (C_6D_6): 1.35 (*t*, J(P,H) = 7.5, Me); −5.87 (*t*, J(P,H) = 21.0, ReH). $^{13}C\{^1H\}$-NMR (C_6D_6): 198.0 (*t*, J(P,C) = 9.9, CO *cis* to H); 197.5 (*t*, J(P,C) = 5.4, CO *trans* to H); 23.8 (*t*, J(P,C) = 33.6, Me). $^{31}P\{^1H\}$-NMR (C_6D_6): −42.0 (*s*). EI-MS: 424 (75, M^+), 396 (100, $[M - CO]^+$), 368 (62, $[M - 2\ CO]^+$). Anal. calc. for $C_9H_{19}O_3P_2Re$: C 25.53, H 4.52; found: C 25.38, H 4.31.

[OC-6-11]-(Benzyloxy)carbonyltetrakis(triphenylphosphine)rhenium(I) ($[Re(CO)(OCH_2Ph)(PMe_3)_4]$; **4**). *trans*-$[ReH(CO)(PMe_3)_4]$ (**3**; 0.35 g, 0.67 mmol) was dissolved in toluene (15 ml) and benzaldehyde (68 µl, 0.67 mmol) added (IR monitoring). After 16 h, the solvent was evaporated and the oily residue extracted with Et_2O (20 ml), and the extract concentrated to 10 ml and slowly cooled to −30° to initiate crystallization of **4**: 0.37 g (89%). IR (hexane): 1803 (CO). ^1H-NMR (C_6D_6): 7.29 (*m*, Ph); 7.19 (*t*, J(H,H) = 7.5, Ph); 7.03 (*t*, J(H,H) = 7.2, Ph); 4.59 (*s*, CH_2O). $^{13}C\{^1H\}$-NMR (C_6D_6): 198.5 (*quint.*, J(P,C) = 8.0, CO); 151.8, 127.3, 125.4, 124.7 (4*s*, Ph); 76.7 (*quint.*, J(P,C) = 3.8, CH_2O); 21.1 (*m*, J(P,C; 1st order) = 31.9, Me). $^{31}P\{^1H\}$-NMR (C_6D_6): −30.6 (*s*). CI-MS: 626 (7, M^+), 550 (100, $[M - PMe_3]^+$), 519 (35, $[M - C_7H_7O]^+$). Anal. calc. for $C_{20}H_{43}O_2P_4Re$: C 38.39, H 6.93; found: C 38.11, H 6.92.

[OC-6-14]-Dicarbonyl[(pyridin-2-yl)methoxy-O,N]bis(trimethylphosphine)rhenium(I) ($[Re\{NC_5H_4(CH_2O)\}(CO)_2(PMe_3)_2]$; **5b**). Pyridine-2-carbaldehyde (81 µl, 0.85 mmol) was added to a soln. of **1** (0.36 g, 0.85 mmol) or of **2** (0.4 g, 0.85 mmol) in CH_2Cl_2 (30 ml) at 0°. After 10 min, the mixture was warmed to r.t. Again after 10 min, the soln. was filtered over silica gel and the filtrate evaporated. Extraction with toluene and crystallization at −30° afforded orange **5b**: 0.42 g (98%). IR (Et_2O): 1908, 1821 (CO). ^1H-NMR (C_6D_6): 8.60 (*d*, J(H,H) = 5.3, H–C(6)); 6.22 (*t*, J(H,H) = 6.5, H–C(5)); 6.75 (*t*, J(H,H) = 7.6, H–C(4)); 6.45 (*d*, J(H,H) = 8.0, H–C(3)); 5.30 (*t*, J(P,H) = 3.5, CH_2O); 1.12 (*t*, J(P,H) = 6.7, Me). $^{13}C\{^1H\}$-NMR (C_6D_6): 205.2 (br. *s*); 203.9 (br. *s*); 173.3 (*s*, C(2)); 150.6 (*s*, C(6)); 135.6 (*s*, C(4)); 121.8 (*s*, C(3)); 118.5 (*s*, C(5)); 77.2 (*s*, CH_2O); 16.3 (*t*, J(P,C) = 27.8). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): −18.0 (*s*). EI-MS: 503 (94, M^+), 475 (100, $[M - CO]^+$), 447 (38, $[M - 2\ CO]^+$), 427 (43, $[M - PMe_3]^+$), 399 (85, $[M - CO - PMe_3]^+$), 371 (17, $[M - 2\ CO - PMe_3]^+$). Anal. calc. for $C_{14}H_{24}NO_3P_2Re$: C 33.46, H 4.81, N 2.79; found: C 33.27, H 4.59, N 3.12.

[OC-6-13]-Dicarbonyl[(pyridin-2-yl)methoxy-O]tris(trimethylphosphine)rhenium(I) ($[Re(OCH_2C_5H_4N)(CO)_2(PMe_3)_3]$; **6a**). Equivalent amounts of **2** and pyridine-2-carbaldehyde were reacted in CD_2Cl_2 at −20° in an

NMR tube to give within complete conversion to **6a**. ^{1}H-NMR (CD_2Cl_2): 8.34 (*m*, H–C(6)); 7.58 (*m*, H–C(3)); 7.51 (*m*, H–C(4)); 6.98 (*m*, H–C(5)); 4.78 (*s*); 1.55 (*t*, *J*(P,H) = 6.4, Me); 1.49 (*d*, *J*(P,H) = 7.1, Me). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 233 K): 200.3 (br. *s*); 199.8 (br. *s*); 170.5 (*s*, C(2)); 147.7 (*s*, C(6)); 135.8 (*s*, C(4)); 120.2 (*s*, C(3)); 119.9 (*s*, C(5)); 81.1 (*d*, *J*(P,C) = 9.3, CH_2O); 18.8 (*dt*, *J*(P,C) = 2.5, *J*(P,C) = 28.6, Me); 17.6 (*dt*, *J*(P,C) = 23.7, *J*(P,C) = 6.6, Me). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 253 K): −30.3 (*d*, *J*(P,P) = 27.1); −30.9 (*t*, *J*(P,P) = 27.1).

[OC-6-11]-Carbonyl[(pyridin-2-yl)methoxy-O]tetrakis(trimethylphosphine)rhenium(I) ([Re($OCH_2C_5H_4N$)(CO)(PMe_3)$_4$]; **7a**). In a NMR tube, equivalent amounts of **3** and pyridine-2-carbaldehyde were mixed at −60° in CD_2Cl_2 to give within complete conversion to **7a**. ^{1}H-NMR (CD_2Cl_2, 213 K): 8.31 (*m*, H–C(6)); 7.62 (*m*, H–C(4)); 7.59 (*m*, H–C(3)); 6.96 (*m*, H–C(5)); 4.60 (*s*, CH_2O); 1.52 (*t*, *J*(P,H) = 4.8, Me). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 233 K): 200.1 (*quint.*, *J*(P,C) = 8.3, CO); 171.1 (*s*, C(2)); 147.3 (*s*, C(6)); 135.8 (*s*, C(4)); 120.0 (*s*, C(3)); 119.8 (*s*, C(5)); 77.9 (*quint.*, *J*(P,C) = 3.5, CH_2O); 20.9 (*m*, *J*(P,C) = 28.6, Me). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 233 K): −29.2 (*s*).

[OC-6-13]-Carbonyl[(pyridin-2-yl)methoxy-O,N]tris(trimethylphosphine)rhenium(I) ([Re($NC_5H_4CH_2O$)(CO)(PMe_3)$_3$]; **7b**). At −60°, pyridine-2-carbaldehyde (86 µl, 0.90 mmol) was added to a soln. of **3** (0.45 g, 0.87 mmol) in CH_2Cl_2 (50 ml). The soln. turned orange within s. After 30 min, the mixture was warmed to r.t. and filtered over *Celite*. Then the solvent was evaporated and the red residue washed with hexane (3 × 20 ml): 0.46 (95%) of **7b**. IR (Et_2O): 1783 (CO). ^{1}H-NMR (CD_2Cl_2, 288 K): 8.92 (*d*, *J*(H,H) = 5.6, H–C(6)); 7.42 (*t*, *J*(H,H) = 7.6, H–C(4)); 6.98 (*d*, *J*(H,H) = 7.7, H–C(3)); 6.81 (*t*, *J*(H,H) = 6.6, H–C(5)); 5.27 (*t*, *J*(P,H) = 2.6, CH_2O); 1.53 (*d*, *J*(P,H) = 7.5, Me); 1.16 (*t*, *J*(P,H) = 5.8, Me). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 288 K): 201.8 (*q*, *J*(P,C) = 7.6, CO); 171.9 (*s*, C(2)); 152.9 (*s*, C(6)); 133.6 (*s*, C(4)); 121.7 (*s*, C(3)); 117.9 (*s*, C(5)); 77.0 (*d*, *J* = 5.6); 24.0 (*d*, *J*(P,C) = 28.3, Me); 17.5 (*t*, *J*(P,C) = 24.8, Me). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 223 K): −21.8 (*d*, *J*(P,P) = 11.6); −22.4 (*t*, *J*(P,P) = 11.6). EI-MS: 551 (27, M^+), 475 (100, $[M - PMe_3]^+$), 399 (83, $[M - 2\,PMe_3]^+$). Anal. calc. for $C_{16}H_{33}NO_2P_2Re$: C 34.91, H 6.04, N 2.54; found: C 34.62, H 5.70, N 2.96.

[OC-6-13]-Dicarbonyl(formato)tris(trimethylphosphine)rhenium(I) ([Re(HCO_2)($CO)_2$(PMe_3)$_3$]; **8**). A soln. of **2** (0.25 g, 0.53 mmol) in toluene (30 ml) was stirred under 1 bar of CO_2 for 2 h. After filtration of the mixture over *Lichroprep* and evaporation, 0.27 g (98%) of colorless crystals of **8** were obtained. IR (hexane): 2836*w* (CH, formate), 1936*s*, 1855*s* (CO), 1621*w* (CO_2). ^{1}H-NMR (C_6D_6): 8.42 (*q*, *J*(P,H) = 1.3, HCO_2); 1.35 (*t*, *J*(P,H) = 6.9, Me); 1.12 (*d*, *J*(H,H) = 7.3, Me). ^{13}C-NMR (C_6D_6): 199.9 (*q*, *J*(P,C) = 6.7, CO); 199.2 (*dt*, *J*(P,C) = 62.0, *J*(P,C) = 9.4, CO); 167.5 (*dt*, *J*(P,C) = 4.7, *J*(P,C) = 2.2, *J*(C,H) = 194, HCO_2); 19.5 (*t*, *J*(P,C) = 30.2, Me); 18.6 (*dt*, *J*(P,C) = 25.3, *J*(P,C) = 5.4, Me). $^{31}P\{^1H\}$-NMR (C_6D_6): −31.3 (*d*, *J*(P,P) = 26.5); −32.7 (*t*, *J*(P,P) = 26.5). EI-MS: 516 (8, M^+), 472 (63, $[M - CO_2]^+$), 440 (100, $[M - PMe_3]^+$), 412 (59, $[M - PMe_3 - CO]^+$). Anal. calc. for $C_{12}H_{28}O_4P_3Re$: C 27.96, H 5.48; found: C 27.74, H 5.14.

[OC-6-11]-Carbonyl(formato)tetrakis(trimethylphosphine)rhenium(I) ([Re(HCO_2)(CO)(PMe_3)$_4$]; **9**). A soln. of **3** (0.4 g, 0.77 mmol) in toluene (30 ml) was placed under 1 bar of CO_2. Within a few s, a precipitate of **9** was formed which was washed with hexane (20 ml): 0.42 g (96%) of **9**. IR (THF): 2812*w* (CH), 1803*s* (CO), 1637*m* (CO_2). ^{1}H-NMR (C_6D_6): 8.22 (*s*, HCO_2); 1.56 (*t*, *J*(P,H) = 5.4, Me). ^{13}C-NMR (C_6D_6): 202.0 (br. *s*, CO); 169.5 (*quint.*, *J*(P,C) = 3.0, *J*(C,H) = 190, HCO_2); 21.6 (*m*, *J*(P,C) = 27.5, Me). ^{31}P-NMR (C_6D_6): −29.1 (*s*). EI-MS: 564 (3, M^+), 520 (43, $[M - CO_2]^+$), 444 (32, $[M - CO_2 - PMe_3]^+$), 416 (100, $[M - CO_2 - PMe_3 - CO]^+$), 340 (27, $[M - CO_2 - 2\,PMe_3 - CO]^+$). Anal. calc. for $C_{14}H_{37}O_3P_4Re$: C 29.84, H 6.62; found: C 29.61, H 6.44.

[OC-6-12]-Tricarbonyl(methyl prop-2-enoate-κC²)bis(trimethylphosphine)rhenium(I) and [OC-6-12]-Tricarbonyl(methyl but-2-enoate-κC²)bis(trimethylphosphine)rhenium(I) ([Re{C(CO_2Me)=CHR}($CO)_3$(PMe_3)$_2$]; **10a** (R = H) and **10b** (R = Me), resp.). To a soln. of **1** (0.5 g, 1.18 mmol) in toluene (40 ml), HC≡CCOOMe (0.17 ml, 3 mmol) or MeC≡CCO_2Me (0.12 ml, 1.30 mmol) was added (reaction times: a few s or 14 d, resp.). After evaporation, the residue was extracted with hexane, the resulting soln. filtered over *Celite* and concentrated. Two crystallizations at −30° afforded 0.57 g (96%) of **10a** and 0.52 g (84%) of **10b**.

10a: IR (hexane): 2034*s*, 1931*s*, 1908*m* (CO), 1697*s* (C=O). ^{1}H-NMR (C_6D_6): 6.65 (*dt*, *J*(H,H) = 4.5, *J*(P,H) = 3.7, H *trans* to Re); 5.60 (*dt*, *J*(H,H) = 4.5, *J*(P,H) = 3.1, H *cis* to Re); 3.51 (*s*, MeO); 1.35 (*t*, *J*(P,H) = 8.0, Me). $^{13}C\{^1H\}$-NMR (C_6D_6): 197.4 (*t*, *J*(P,C) = 5.8, CO); 196.7 (*t*, *J*(P,C) = 9.5, CO *trans*); 182.8 (*s*, CO_2Me); 158.1 (*t*, *J*(P,C) = 12.1, Re–C); 128.4 (*t*, *J*(P,C) = 4.9, CH_2); 50.9 (*s*, MeO); 20.0 (*t*, *J*(P,H) = 33.8, Me). $^{31}P\{^1H\}$-NMR (C_6D_6): −40.1 (*s*). EI-MS: 508 (60, M^+), 480 (25, $[M - CO]^+$), 452 (42, $[M - 2\,CO]^+$), 424 (11, $[M - 3\,CO]^+$), 396 (100, $[M - CO - C_4H_4O_2]$). Anal. calc. for $C_{13}H_{23}ReO_3P_2$: C 30.77, H 4.57; found: C 30.54, H 4.76.

10b: IR (hexane): 2031*w*, 1927*s*, 1906*m*, 1695*w* (C=O). ^{1}H-NMR (C_6D_6): 6.49 (*qt*, *J*(H,H) = 6.5, *J*(C,H) = 3.8, =CH); 3.50 (*s*, MeO); 1.78 (*dt*, *J*(H,H) = 6.5, *J*(P,H) = 2.4, =CH*Me*); 1.39 (*t*, *J*(P,H) = 7.8, Me). ^{13}C-NMR (C_6D_6): 196.7 (*t*, *J*(P,C) = 9.6, CO); 194.8 (*t*, *J*(P,C) = 5.5, CO); 194.0 (*t*, *J*(P,C) = 9.3, CO); 182.3 (*s*, ^3J(C,H) = 8.4, CO_2Me); 149.7 (*t*, *J*(P,C) = 12.6, Re–C); 133.9 (*t*, *J*(P,C) = 4.7, ^1J(C,H) = 149.0, =*C*HMe); 49.9 (*s*, MeO); 22.8 (*s*, =CH*Me*); 19.9 (*t*, *J*(P,C) = 33.8, Me). $^{31}P\{^1H\}$-NMR (C_6D_6): −39.9 (*s*). EI-MS: 522 (93, M^+),

494 (24, $[M - CO]^+$), 466 (80, $[M - 2\,CO]^+$), 438 (12, $[M - 3\,CO]^+$), 424 (53, $[M - C_5H_6O_2]^+$), 410 (65), 395 (100, $[M - CO - C_5H_7O_2]^+$), 367 (38, $[M - 2\,CO - C_5H_7O_2]^+$), 362 (34, $[M - 3\,CO - PMe_3]^+$). Anal. calc. for 521.5: C 32.24, H 4.83; found: C 32.46, H 4.70.

The same reaction was pursued by ^{1}H-NMR in C_6D_6, whereby resonances of **10c** were detected.

[OC-6-12]-Tricarbonyl(methyl but-2-enoate-κC^3)bis(trimethylphosphine)rhenium(I) (**10c**): ^{1}H-NMR (C_6D_6): 8.88 (*dt*, J(H,H) = 14.8, J(P,H) = 4.6, ReC*H*); 7.39 (*dt*, J(H,H) = 14.8, J(P,H) = 3.4, ReCH=C*H*); 3.54 (*s*, MeO); 1.28 (*t*, J(P,H) = 7.6, Me).

[OC-6-12]-Dicarbonyl(methyl prop-2-enoate-κC^2)bis(trimethylphosphine)rhenium(I) ([Re{C(CO_2Me)=CH_2}-$(CO)_2(PMe_3)_2$]; **11**). At r.t., **2** (0.13 g, 0.28 mmol) and HC≡CCOMe (25 µl, 0.28 mmol) were dissolved in toluene (10 ml). After filtration over *Celite*, the solvent was evaporated and the pale yellow residue washed with cold hexane until it became colorless: 0.15 g (97%) of **11**. IR (toluene): 1930*s*, 1850*s* (CO), 1695*w* (C=O). ^{1}H-NMR (C_6D_6): 6.48 (*ddt*, J(H,H) = 4.8, J(P,H) = 2.3, 3.7, H *trans* to Re); 5.30 (*dt*, J(H,H) = 4.8, J(P,H) = 3.1, H *cis* to Re); 3.59 (*s*, MeO); 1.45 (*t*, J(P,H) = 7.1, Me); 1.12 (*d*, J(P,H) = 6.9, Me). ^{13}C{^{1}H}-NMR (C_6D_6): 199.7 (*dt*, J(P,C) = 9.3, 6.4, CO); 199.4 (*dt*, J(P,C) = 56.2, 9.4, CO); 182.5 (*d*, J(P,C) = 4.3, *C*O_2Me); 162.6 (*dt*, J(P,C) = 10.3, 12.4, Re–C); 124.4 (*dt*, J(P,C) = 9.7, 4.7, =CH_2); 49.9 (*s*, MeO); 20.3 (*dt*, J(P,C) = 30.6, 2.1, Me); 20.5 (*dt*, J(P,C) = 26.0, 5.2, Me). ^{31}P{^{1}H}-NMR (C_6D_6): −42.8 (*d*, J(P,P) = 26.7); −49.1 (*t*, J(P,P) = 26.7). EI-MS: 556 (36, M^+), 480 (78, $[M - PMe_3]^+$), 452 (68, $[M - PMe_3 - CO]^+$), 424 (11, $[M - PMe_3 - 2\,CO]^+$), 396 (100, $[M - PMe_3 - C_4H_4O_2]^+$). Anal. calc. for $C_{15}H_{32}O_4P_2Re$: C 32.34, H 5.81; found: C 32.15, H 5.74.

[OC-6-11]-Carbonyl(methyl prop-2-enoate-κC^2)tetrakis(trimethylphosphine)rhenium(I) ([Re{C(CO_2Me)=CH_2}-$(CO)(PMe_3)_4$]; **12**). A soln. of **3** (0.55 g, 1.06 mmol) and HC≡CCO_2Me (0.11 ml, 1.2 mmol) in toluene (40 ml) was stirred for 4 h at r.t. The colourless soln. was filtered over *Celite* and the filtrate evaporated: **12** (0.60 g, 93%). White powder. IR (Et_2O): 1815*s* (CO), 1697*w* (C=O). ^{1}H-NMR (C_6D_6): 6.47 (*d quint.*, J(H,H) = 5.6, J(P,H) = 1.0, H *trans* to Re); 5.49 (*d quint.*, J(H,H) = 5.6, J(P,H) = 1.6, H *cis* to Re); 3.43 (*s*, MeO); 1.46 (*t*, J(P,H) = 5.3, Me). ^{13}C{^{1}H}-NMR (C_6D_6): 202.2 (*quint.*, J(P,C) = 9.9, CO); 184.0 (*quint.*, J(P,C) = 2.2, *C*O_2Me); 163.6 (*quint.*, J(P,C) = 11.4, Re–C); 128.7 (*quint.*, J(P,C) = 6.9, =CH_2); 50.1 (*s*, CO_2Me); 23.0 (*m*, J(P,C) = 29.6, Me). ^{31}P{^{1}H}-NMR (C_6D_6): −43.8 (*s*). EI-MS: 604 (4, M^+), 528 (76, $[M - PMe_3]^+$), 452 (33, $[M - 2\,PMe_3]^+$), 424 (15, $[M - 2\,PMe_3 - CO]^+$), 396 (100). Anal. calc. for $C_{17}H_{41}O_3P_4Re$: C 33.83, H 6.85; found: C 33.61, H 6.70.

[OC-6-12]-Dicarbonyl[methyl (Z)- and (E)-but-2-enoate-κC^2]tris(trimethylphosphine)rhenium(I) ([Re{(*Z*)- and (*E*)-C(CO_2Me)=CHMe}$(CO)_2(PMe_3)_3$]; **13a** and **13b**, resp.). A soln. of **2** (0.35 g, 0.74 mmol) and MeC≡CCO_2Me in toluene (15 ml) was evaporated after 7 h. The mixture **13a**/**13b** was purified by recrystallization from hexane at −30°: **13a**/**13b** (0.14 g, 94%). IR (hexane): 1933*s*, 1855*s* (CO), 1697*w* (C=O). EI-MS: 570 (26, M^+), 494 (81, $[M - PMe_3]^+$), 466 (62, $[M - PMe_3 - CO]^+$), 395 (100, $[M - PMe_3 - C_5H_7O_2]^+$). Anal. calc. for $C_{16}H_{34}O_4P_3Re$: C 33.74, H 6.02; found: C 33.40, H 6.18.

13a: ^{1}H-NMR (C_6D_6): 6.71 (*qdt*, J(H,H) = −6.5, J(P,H) = 1.3, 3.8, =CH); 3.38 (*s*, MeO); 2.08 (*dt*, J(H,H) = 6.5, J(P,H) = 2.3, =CHMe); 1.44 (*t*, J(P,H) = 7.0, Me); 1.23 (*d*, J(P,H) = 7.1, Me). ^{13}C-NMR (C_6D_6): 200.7 (*dt*, J(P,C) = 55.7, 10.4, CO); 199.6 (*dt*, J(P,C) = 8.1, 6.9, CO); 183.4 (*d*, J(P,C) = 6.4, ^3J(C,H) = 9.1, *C*O_2Me); 153.6 (*dt*, J(P,C) = 9.2, 13.0, Re–C); 137.2 (*dt*, J(P,C) = 6.6, 4.6, ^1J(C,H) = 156.3, =CH); 50.3 (*s*, MeO); 23.3 (*s*, =CH*Me*); 21.4 (*dt*, J(P,C) = 1.6, 30.2, Me); 20.9 (*dt*, J(P,C) = 24.2, 4.6, Me). ^{31}P{^{1}H}-NMR (C_6D_6): −40.2 (*d*, J(P,P) = 26.4); −53 (*t*, J(P,P) = 26.4).

13b: ^{1}H-NMR (C_6D_6): 5.37 (*qt*, J(H,H) = 6.2, J(P,H) = 3.1, =CH); 3.62 (*s*, MeO); 1.81 (*dt*, J(H,H) = 6.2, J(P,H) = 3.0, =CH*Me*); 1.45 (*t*, J(P,H) = 7.0, Me); 1.13 (*d*, J(P,H) = 6.8, Me). ^{13}C-NMR (C_6D_6): 199.6 (*dt*, J(P,C) = 8.1, 6.9, CO); 199.5 (*dt*, J(P,C) = 56.1, 9.8, CO); 181.4 (*d*, J(P,C) = 4.3, ^3J(C,H) = 16.6, *C*O_2Me); 151.8 (*dt*, J(P,C) = 10.2, 12.7, Re–C); 129.4 (*dt*, J(P,C) = 9.8, 5.1, =CHMe, ^1J(C,H) = 156.3, =CH); 49.1 (*s*, MeO); 20.6 (*dt*, J(P,C) = 1.6, 30.4, Me); 20.5 (*dt*, J(P,C) = 27.0, 5.0, Me). ^{31}P{^{1}H}-NMR (C_6D_6): −41.6 (*d*, J(P,P) = 26.8); −49.5 (*t*, J(P,P) = 26.8).

[OC-6-11]-Carbonyl[methyl (E)-but-2-enoate-κC^2]tetrakis(trimethylphosphine)rhenium(I) ([Re{(*E*)-C(CO_2Me)=CHMe}$(CO)(PMe_3)_4$]; **14**). As described for **12**, **3** (0.5 g, 0.96 mmol) and MeC≡CCO_2Me (0.16 ml, 1 mmol) were reacted for 1 h: 0.56 g (95%) **14**. IR (Et_2O): 1811*s* (CO), 1690*w* (C=O). ^{1}H-NMR (C_6D_6): 5.6 (*qquint.*, J(H,H) = 6.3, J(P,H) = 1.6, =CH); 3.41 (*s*, MeO); 1.72 (*dquint.*, J(H,H) = 6.3, J(P,H) = 1.6, =CH*Me*); 1.45 (*t*, J(P,H) = 5.3, Me). ^{13}C-NMR (C_6D_6): 201.7 (*quint.*, J(P,C) = 9.9, CO); 182.7 (*quint.*, J(P,C) = 2.0, ^3J(C,H) = 16.3, *C*O_2Me); 151.6 (*quint.*, J(P,C) = 11.5, Re–C); 134.2 (*quint.*, J(P,C) = 7.4, ^1J(C,H) = 154.7, =CH); 51.8 (*s*, MeO); 23.1 (*s*, =CH*Me*); 22.9 (*m*, J(P,C) = 28.0, Me). ^{31}P{^{1}H}-NMR (C_6D_6): −43.6 (*s*). CI-MS: 618 (6, M^+), 542 (100, $[M - PMe_3]^+$), 466 (43, $[M - 2\,PMe_3]^+$). Anal. calc. for $C_{18}H_{43}O_3P_4Re$: C 35.00, H 7.02; found: C 34.81, H 6.74.

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