105. The Vinylidene/Acyl Coupling at Rhenium Centers

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The reaction of $[Re(CO_3)L_2Cl]$ (L = $(MeO)_3P$, **1a**; L = $(i\text{-}PrO)_3P$, **1b**; L = $(PhO)_3P$, **1c**; L = Me_3P, **1d**; L = Et_3P, **1e**) with *t*-BuLi and phenylacetylene in THF affords bis(phosphorus donor)(dicarbonyl){η^2(C,O)-[(*E*)-4,4-dimethyl-3-oxo-1-phenylpent-1-en-2-yl]}rhenium (L = $(MeO)_3P$, **2a**; L = $(i\text{-}PrO)_3P$, **2b**; L = $(PhO)_3P$, **2c**; L = Me_3P, **2d**; L = Et_3P, **2e**). Compounds **2b** and **2d** were characterized by X-ray structure analysis.

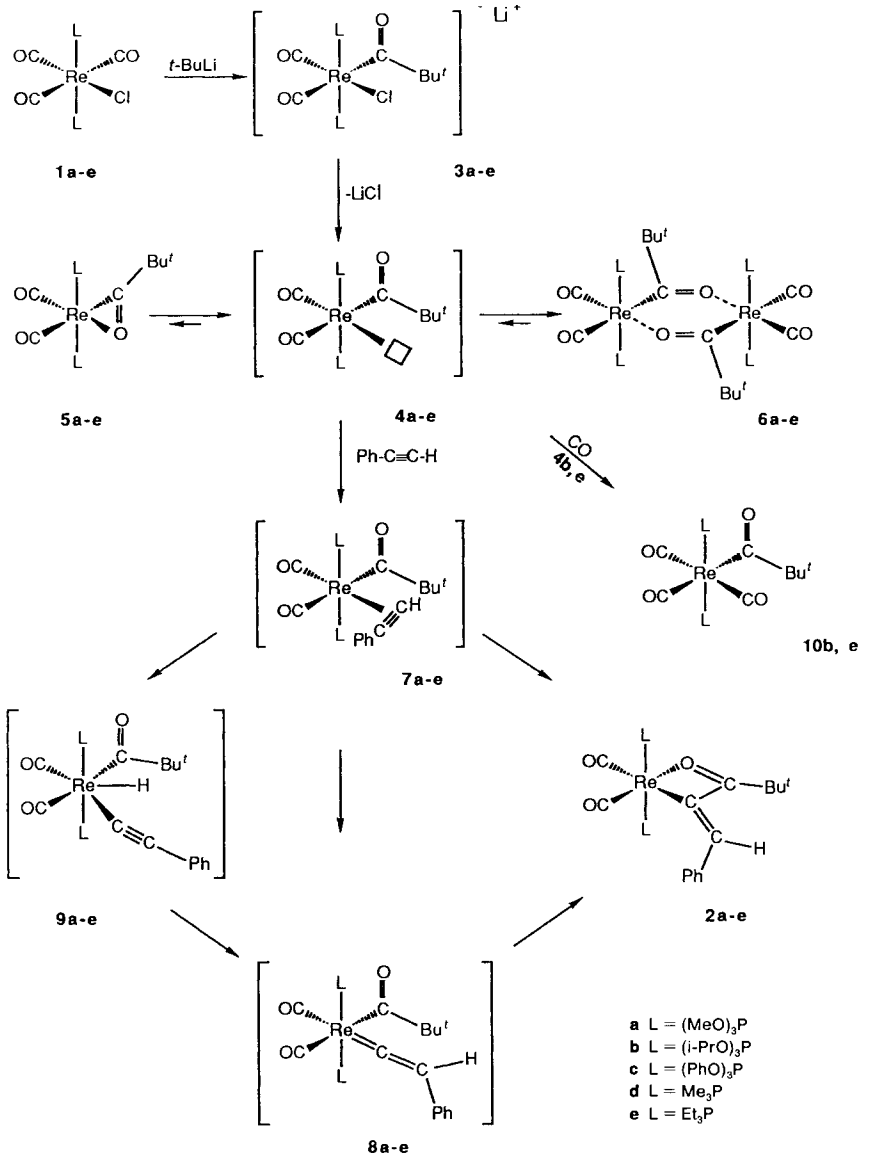
Introduction. – Acetylenes are versatile and quite common reagents for transition-metal-mediated C–C coupling reactions. Normally, the acetylene unit participates in cyclisations or oligomerisations as a C_2 building block [1], and it is a relatively rare but nevertheless desirable case, that the acetylene provides just one C-atom for such chain- or ring-forming processes. Typically, the latter transformations are observed with terminal acetylenes which show great disposition for the acetylene/vinylidene rearrangement [2]. The vinylidene unit behaves as an electrophilic carbene ligand, and can as such undergo coupling with metal-coordinated nucleophiles. In this paper, we report on the transition-metal-induced conversion of acyl and vinylidene ligands to produce α-acylvinyl moieties, simply starting from a terminal acetylene, an alkyl-lithium reagent, and $[Re(CO)_3L_2Cl]$ (L = phosphorus donor).

Results and Discussion. – According to *Scheme 1*, the addition of *t*-BuLi to $[Re(CO_3)L_2Cl]$ (L = $(MeO)_3P$, **1a**; L = $(i\text{-}PrO)_3P$, **1b**; L = $(PhO)_3P$, **1c**; L = Me_3P, **1d**; L = Et_3P, **1e**) in THF or Et_2O at −78° with subsequent introduction of 1 equiv. of phenylacetylene results in the formation of bis(phosphorus donor)(dicarbonyl){η^2(C,O)-[(*E*)-4,4-dimethyl-3-oxo-1-phenylpent-1-en-2-yl]}rhenium complexes (L = $(MeO)_3P$, **2a**; L = $(i\text{-}PrO)_3P$, **2b**; L = $(PhO)_3P$, **2c**; L = Me_3P, **2d**; L = Et_3P, **2e**). The yellow-to-red crystalline compounds **2a–e** have been isolated in moderate-to-good yields, in most cases with preceding column chromatography.

Although **2a–e** represent cyclic systems with a supposedly high ring strain, they appear quite inert. This is demonstrated by the inability of **2** to react with CO in hexane at room temperature.

The determination of the structures of compounds **2** is based on the X-ray structure analysis of **2b** and **2d** and their spectroscopic properties which show great similarities for all congeners. The IR spectra of **2** (range 2000–1800 cm^{-1}) are characterized by two ν(C≡O) absorptions. It should be mentioned that it was not possible to assign ν(C=O) bands for **2** probably due to their overlap with absorptions of aromatic ν(C–C) vibrations. The ^{1}H-NMR spectra of compounds **2** exhibited a low-field *triplet* in a region typical of vinylic protons with the specific stereochemical environment as in **2** [2a]. Thus, these nuclei absorb *ca.* 3 ppm more downfield than *exo*-methylidene protons which are

Scheme 1



attached to five-membered rhenadihydrofuran rings [2b]. Among the ^{13}C-NMR resonances for compounds **2**, it is noteworthy that the $C_{carbonyl}$ of the pivaloyl group appear at remarkably constant chemical-shift values between 232 and 237 ppm which emphasizes great similarity of the electronic and topological properties of all derivatives. In accord with the IR spectroscopic evidence and the postulated configuration at the Re center, two ^{13}C-NMR signals for chemically inequivalent CO ligands are observed.

Following *Scheme 1*, it is expected that the reaction from **1** to **2** would proceed *via* initial attack of a *t*-Bu anion on a CO ligand in **1** to form the pivaloyl moieties of **3**. These species then loose a Cl^- ion to yield the short-lived 16-electron intermediates **4** which are suggested to undergo either internal stabilization *via* η^2-acyl binding as in **5** or dimerize to produce **6**. In the case of the reaction of **1b** with *t*-BuLi without further addition of phenylacetylene, a white microcrystalline solid was isolated, which we believe has the structure of either **5b** or **6b**. From spectroscopic evidence (^{31}P- and ^{13}C-NMR), the product from this reaction of **1b** has to be considered a single component. The available NMR data are, however, not sufficient to provide distinction between structure **5b** or **6b**. The ^{13}C-NMR resonance at 305.6 ppm indicates the presence of an η^2-bound CO group. It falls into the relatively wide absorption range of mononuclear and bridging binding modes of pivaloyl moieties [3] and, thus, supports both isomeric arrangements. In the mass spectra of this compound, the peak with the highest mass corresponds to the molecular weight of **5b**. But, due to the general uncertainty in the assignment of molecular weights from molecular peaks, the existence of **6b** cannot be ruled out. Unfortunately, crystals suitable of X-ray analysis were not obtained. The structure of an unsubstituted analogue of **6**, μ-[2,4,6-tri(*tert*-butyl)phenylcarbonyl]$_2$[Re(CO)$_4$]$_2$ which was synthesized by a different route, has been determined by X-ray diffraction [4]. The white precipitate of **5b** or **6b** easily reacts with CO in hexane to produce bis(triisopropoxyphosphine)tricarbonyl(pivaloyl)rhenium **10b**. This stresses the existence of a facile equilibrium leading to the 16-electron species **4b**, but again does not give clear preference to either **5b** or **6b** as the starting component.

Compound **4** and implicitly **5** or **6** can pick up phenylacetylene to give the derivatives **7**; it is important to note that the well-characterized μ-(MeCO)$_2$[Re(CO)$_4$]$_2$ complex [3a], being isostructural to **6**, does not react with phenylacetylene in THF at room temperature. This may be taken as a chemical hint to give preference to the presence of species **5** over **6** in the equilibrium with **4**. It should, however, be clear that the chemical behavior of phosphorus-donor-substituted compounds of type **6** do not necessarily follow the lines of the parent carbonyl complexes.

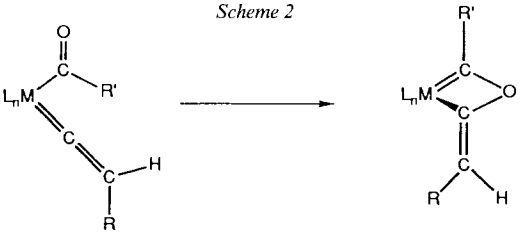
Three alternative routes would lead from **7** to the final product **2**: *a*) primary oxidative addition of the acetylenic C–H bond to the Re center and subsequent β-hydrogen transfer to yield vinylidene compounds **8**, which would then transform by α-pivaloyl migration to **2**; *b*) direct acetylene/vinylidene prototropic rearrangement to **8**, following then route *a*; *c*) acetylene/vinylidene conversion and pivaloyl migration are coupled in a synchronous way.

For none of these routes *a–c*, there is obvious experimental evidence. *Path b* has been checked theoretically on an (acetylene)(acyl)iron model [2a]. It was concluded that the formation of species like **8** is energetically not favorable, but their intermediacy can be circumvented by a process following *Path c*. Since in this case acyl attack and proton migration have to occur at the same side of the C=C bond, a (*Z*)-substitution pattern of these residues should result. For **2**, we exclusively find the isomer with (*Z*)-configuration, which would support the assumption of a simultaneous movement of both groups along *Path c*. In closely related vinylidene/carbanion coupling reactions [2b], *Bergman* and coworkers have, however, spectroscopically detected products with an (*E*)-configuration of the moving substituents as minor components so that it remains unclear which of the *Paths a–c* is relevant for the reactions **7** → **2**.

Having outlined plausible mechanistic pathways for the conversion **1** → **2**, the important question arises, why the transformation sequence is such as it appears. Compounds of type **7** should, in principle, show great propensity to undergo the well-documented direct acyl/acetylene coupling [5]. The reason for the obvious absence of this elementary step in the transformation sequence starting from **7** is unclear. This may, on the one hand, be caused by specific electronic factors of the $[Re(CO)_2L_2]$ fragments which support formation of vinylidene ligands. On the other hand, the acyl/acetylene coupling is obviously disfavored in these specific systems, since it is observed that mixtures of *t*-BuLi and **1** are reluctant to react with internal acetylenes, like phenylpropyne.

According to *Scheme 2*, an alternative type of reaction channel compared to that one shown in *Scheme 1* exists for vinylidene acyl complexes like **8**. This process is a well known type of transformation in the realm of Ru and Os acyl carbene chemistry [6].

Scheme 2



The reason why compounds **8** do not make use of the reaction given in *Scheme 2*, leading to isomers of **2**, could be related to the steric bulkyness of the *t*-Bu group which has to face enhanced repulsion in proximity to the Re center. Moreover, if the Re-atom is assumed to be of higher oxophilicity than Ru or Os, arrangements with a Re–O contact would thermodynamically be favored.

X-Ray Structure of 2b and 2d. – Structural investigation of metallaoxetanes or metallaoxetenes are quite rare [2] [6]. They often reveal unexpected features due to unusual electronic properties and the strain situation in the ring system. To gain further insight into the stuctural properties of Re derivatives of this class of compounds, X-ray structure analyses on **2b** and **2d** were carried out.

Crystals suitable for this purpose were obtained by recrystallization from hexane (for **2b**) or hexane/Et_2O (for **2d**) at −30°. (For crystal, structure-solution, and refinement data of **2b** and **2d**, see the *Table*.) In the structure of **2d**, rotational disorder of the Me groups of the Me_3P ligands was observed, which in the structure-solution and refinement procedure was accounted for by fitting with topological models and appropriate site occupancy factors.

From the *Figure*, it can be seen that **2b** and **2d** show pseudo-octahedral coordination around the Re center. The Re–O=C–C moieties are nearly planar and exhibit only minor deviations from the expected bond lengths in the organic part (**2b**: C(11)–O(3), 128.0(11) pm; C(3)–C(11), 147.6(12) pm; **2d**: C(11)–O(3), 128.0(15) pm; C(3)–C(11), 147.8(14) pm). The Re–O contacts appear to be quite weak (**2b**: Re–O(3), 222.4(6) pm; **2d**: Re–O(3), 223.7(6) pm) compared to Re–$O_{enolate}$ separations which lie between 190 and 195 pm [7]. It may, therefore, be suggested, that the Re–O bonds carry to some extend strain of the rhenaoxetene unit, which is, however, somewhat contrasted by the inert chemical behavior of these compounds.

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

	2b	**2d**
Empirical formula	$C_{33}H_{57}O_9P_2Re$	$C_{21}H_{33}O_3P_2Re$
Color; habit	yellow, irregular	dark red prism
Crystal size (mm)	0.3 × 0.3 × 0.1	0.54 × 0.14 × 0.21
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a [Å]	11.789(3)	16.773(6)
b [Å]	35.353(8)	8.975(3)
c [Å]	9.833(3)	17.336(6)
β [°]	104.86(2)	113.05(3)
V [Å^3]	3961(2)	2401.4(14)
Z	4	4
Formula weight	845.9	581.6
$D_{calc.}$ [Mg/m^3]	1.418	1.609
Absorption coefficient [mm^{-1}]	3.231	5.276
F(000)	1728	1152
Solution	Direct methods	*Patterson*
System used	*Siemens* SHELXTL PLUS	*Siemens* SHELXTL PLUS
Diffractometer used	*Siemens R3m/V*	*Siemens R3m/V*
Radiation	MoK_α (λ = 0.71073 Å)	MoK_α (λ = 0.71073 Å)
Temp. [K]	209	235
Monochromator	Highly oriented graphite crystal	
2θ Range	3.0 to 58.0°	4.0 to 55.0°
Scan type	*Wyckoff*	*Wyckoff*
Scan speed	Variable; 1.50 to 15.00°/min in ω	Variable; 2.00 to 15.00°/min in ω
Scan range (ω)	1.00°	1.20°
Independent reflections	10554 (R_{int} = 9.97%)	5529 (R_{int} = 7.26%)
Observed reflections	9008 ($F > 6.0\sigma(F)$)	4429 ($F > 6.0\sigma(F)$)
Absorption correction	Semi-empirical	Semi-empirical
Min./Max. transmission	0.0159/0.0428	0.0706/0.1395
R	7.15%	5.93%
wR	7.32%	6.37%

Judging the C–C angles of the α-acylvinyl group which do not deviate much from the expected 120° at the C-atoms, it seems obvious that the C–C backbone is quite rigid and maybe structure-determining. Greater structural flexibility necessary to constitute the four-membered ring is provided by the $(C–C–O)_{acyl}$ angles (**2b**: C(3)–C(11)–O(3), 110.4(7)°; **2d**: C(3)–C(11)–O(3), 109.6(8)°).

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Experimental Part

General. All manipulations were carried out under dry N_2 and solvents dried and distilled under N_2 before use. For chromatographic separations, columns (∅ 3 cm) with silica gel (20 cm, *Merck*) thermostated at –10 to –20° were used. Solvents were used as purchased. *Lichroprep Si 60* (*Merck*) served as a filter aid. FT-IR: *Biorad FTS 45*. FT-NMR: *Varian Gemini 200*, *Varian Gemini 300*, and *Bruker AC-300*. MS: *Finnigan MAT 8240*.

Starting Materials. [$Re(CO)_5Cl$] was prepared by a slight modification of the published procedure [8]. Instead of C_6H_6, CH_2Cl_2 was used for the extraction in a *Soxhlett* apparatus. [$Re(CO)_3L_2Cl$] (**1a–e**) were prepared by

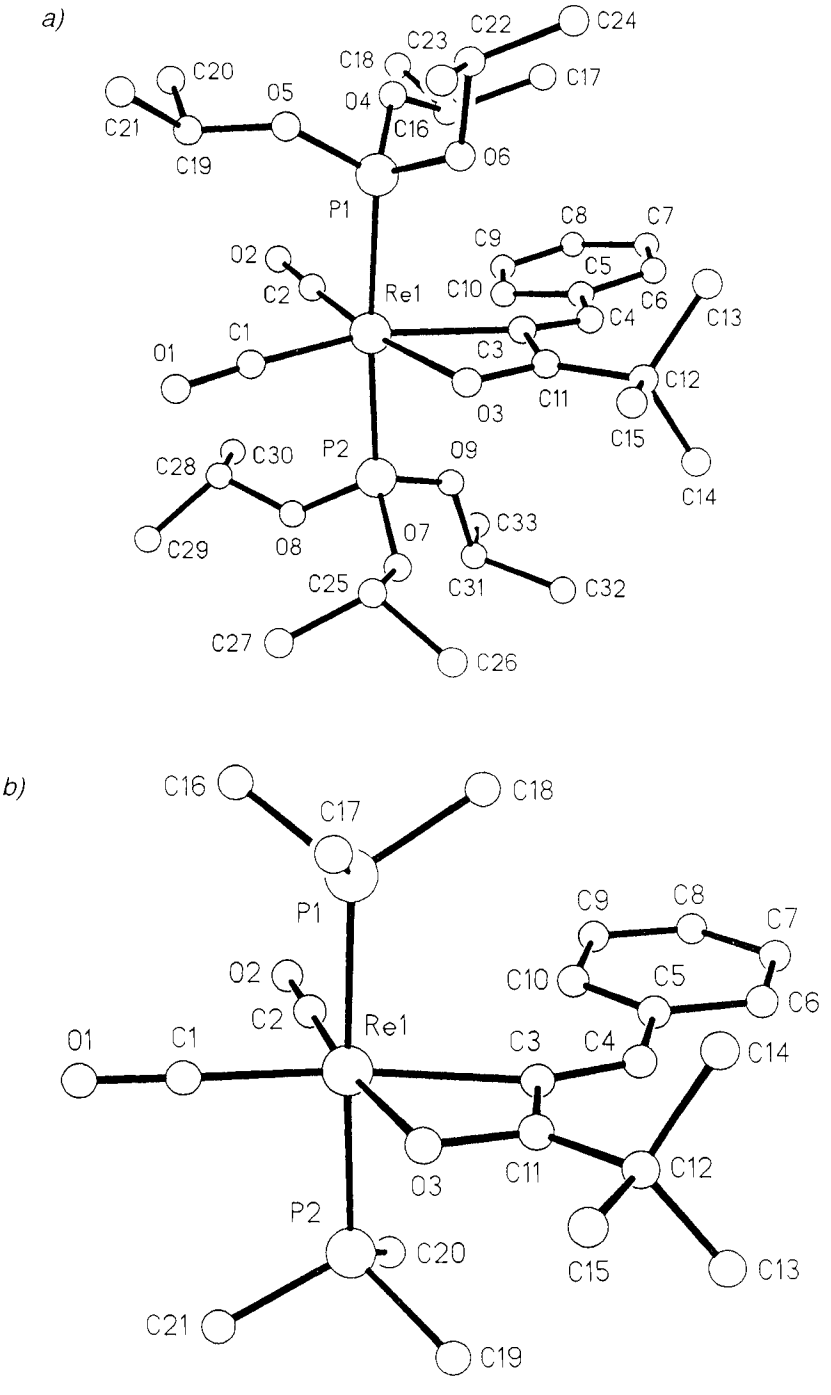

Figure. *Structure models of the compounds* **2b** (a) *and* **2d** (b)

addition of 2 equiv. of L in a soln. of toluene with $[Re(CO)_5Cl]$ and a catalytic amount of $NaBH_4$ in analogy to a published procedure [9].

Synthesis of Bis(phosphorus donor)(dicarbonyl){η²(C,O)-[(E)-4,4-dimethyl-3-oxo-1-phenylpent-1-en-2-yl]}rhenium (L = $(MeO)_3P$, **2a**; L = $(i\text{-}PrO)_3P$, **2b**; L = $(PhO)_3P$, **2c**; L = Me_3P, **2d**; L = Et_3P, **2e**). A soln. of **1** (1.4 mmol) in THF (150 ml) was treated with *t*-BuLi (1 ml 1.4 mmol) at −80°. The color immediately changed to yellow. After 30 min, phenylacetylene (0.2 ml, 1.4 mmol) was added and the mixture allowed to warm up to r.t. The soln. was evaporated to dryness, the solid residue extracted with a small amount of hexane and chromatographed over silica gel (toluene). Recrystallization from hexane at −30° yielded yellow or red crystals of **2**.

Bis(trimethoxyphosphine)(dicarbonyl){η²(C,O)-[(E)-4,4-dimethyl-3-oxo-1-phenylpent-1-en-2-yl]}rhenium (**2a**). The product was extracted with CH_2Cl_2 and chromatographed with hexane/Et_2O 4:1. Recrystallization from hexane afforded yellow crystals. Yield 40%. IR (hexane): 1942, 1864 (C≡O). ^{1}H-NMR (C_6D_6): 1.32 (*s*, $(CH_3)_3C$); 3.40 (*t*, *J*(P,H) = 11.0, 2 $(MeO)_3P$); 7.17–7.24, 7.35–7.42, 8.11–8.15 (*m*, Ph); 9.18 (br. *s*, =CH). ^{13}C-NMR (C_6D_6): 28.2 (*s*, $(CH_3)_3C$); 46.6 (*s*, $(CH_3)_3C$); 51.3 (*s*, $(MeO)_3P$); 129.0, 129.1, 141.6, 142.9 (*s*, Ph); 150.9 (*s*, CHPh); 152.2 (*t*, *J*(P,C) = 14.7, ReC); 201.7 (*t*, *J*(P,C) = 11.9, CO); 201.8 (*t*, *J*(P,C) = 10.0, CO); 234.6 (*t*, *J*(P,C) = 2.8, $COC(CH_3)_3$). ^{31}P-NMR (C_6D_6): 140.0. MS: 678 (32, M^+), 650 (8, $[M - CO]^+$), 622 (38, $[M - 2\ CO]^+$), 526 (8, $[M - CO - P(OMe)_3]^+$), 498 (12, $[M - 2\ CO - P(OMe)_3]^+$). Anal. calc. for $C_{21}H_{33}O_3P_2Re$ (677.6): C 37.22, H 4.91, Re 27.48; found: C 36.98, H 5.11, Re 27.10.

Bis(triisopropoxyphosphine)(dicarbonyl){η²(C,O)-[(E)-4,4-dimethyl-3-oxo-1-phenylpent-1-en-2-yl]}rhenium (**2b**). Yellow crystals. Yield 70%. IR (hexane): 1933, 1851 (C≡O). ^{1}H-NMR (C_6D_6): 1.17 (*d*, *J*(H,H) = 6.1, 3 $OCH(CH_3)_2$); 1.23 (*d*, *J*(H,H) = 6.1, 3 $OCH(CH_3)_2$); 1.44 (*s*, $(CH_3)_2C$); 4.83 (*m*, *J*(H,H) = 6.1, 6 POCH); 7.17–7.21 (*m*, 1 H, Ph); 7.31–7.39 (*m*, 2 H, Ph); 8.06–8.11 (*m*, 2 H, Ph); 9.20 (*t*, *J*(P,H) = 2.2, =CH). ^{13}C-NMR ($CDCl_3$): 23.9 (*s*, $OCH(CH_3)_2$); 28.5 (*s*, $(CH_3)_3C$); 46.1 (*s*, $(CH_3)_3C$); 127.6, 128.2, 129.3, 141.2 (*s*, Ph); 149.8 (*s*, CHPh); 154.5 (*t*, *J*(P,C) = 14.2, ReC); 202.8 (*t*, *J*(P,C) = 11.4, CO); 203.4 (*t*, *J*(P,C) = 10.2, CO); 234.0 (*s*, $COC(CH_3)_3$). ^{31}P-NMR (C_6D_6): 132.9. MS: 846 (100, M^+), 818 (40, $[M - CO]^+$), 788 (76, $[M - CO - 2\ CH_3]^+$), 760 (16, $[M - 2\ CO - 2\ CH_3]^+$), 639 (10, $[M - P(OiC_3H_7)_3]^+$). Anal. calc. for $C_{33}H_{57}O_9P_2Re$ (846.0): C 46.79, H 6.79, Re 22.01; found: C 47.00, H 6.57, Re 21.88.

Bis(triphenoxyphosphine)(dicarbonyl){η²(C,O)-[(E)-4,4-dimethyl-3-oxo-1-phenylpent-1-en-2-yl]}rhenium (**2c**). The product was extracted with CH_2Cl_2, for chromatography a mixture of hexane/CH_2Cl_2 2:1 was used and recrystallized from hexane. Yellow crystals. Yield 50%. IR (CH_2Cl_2): 1956, 1876 (C≡O), 1590, 1490 (Ph). ^{1}H-NMR ((D$_6$)ether): 1.26 (*s*, $(CH_3)_3C$); 6.78–7.37, 8.20–8.24 (*m*, 35 H, Ph, PhO); 9.45 (*t*, *J*(P,H) = 2.1, =CH). ^{13}C-NMR (C_6D_6): 28.3 (*s*, $(CH_3)_3C$); 47.0 (*s*, $(CH_3)_3C$); 127.8, 128.3, 129.4, 129.6 (*s*, Ph); 121.4, 124.6, 129.7 (*s*, PhO); 140.8 (*s*, =CHPh); 149.6 (*t*, *J*(P,C) = 15.3, ReC); 152.3 (*t*, *J*(P,C) = 3.9, P–O–C); 198.6 (*t*, *J*(P,C) = 9.2, CO); 199.8 (*t*, *J*(P,C) = 12.7, CO); 236.5 (*s*, *J*(P,C) = 2.2, $COC(CH_3)_3$). ^{31}P-NMR (C_6D_6): 118.6. MS: 1050 (32, M^+), 1022 (12, $[M - CO]^+$), 996 (5, $[M - 2CO]^+$). Anal. calc. for $C_{51}H_{45}O_9P_2Re$ (1050.1): C 58.34, H 4.32, Re 17.73; found: C 57.99, H 4.43, Re 16.64.

Bis(trimethylphosphine)(dicarbonyl){η²(C,O)-[(E)-4,4-dimethyl-3-oxo-1-phenylpent-1-en-2-yl]}rhenium (**2d**). The reaction was carried out in Et_2O. The final mixture was filtered over *Celite*. Compound **2d** was recrystallized from hexane/Et_2O. Red crystals. Yield 70%. IR (hexane): 1920, 1841 (C≡O). ^{1}H-NMR (C_6D_6): 1.19 (*s*, $(CH_3)_3C$); 1.19 (*t*, *J*(P,H) = 6.8, $(CH_3)_3P$); 7.19–7.24, 7.36–7.44, 8.09–8.13 (*m*, Ph); 9.11 (*t*, *J*(P,H) = 2.6, =CH). ^{13}C-NMR ($CDCl_3$): 17.8 (*t*, *J*(P,C) = 15.1, $(CH_3)_3P$); 28.8 (*s*, $(CH_3)_3C$); 46.7 (*s*, $(CH_3)_3C$); 128.1, 128.5, 128.9, 141.0 (*s*, Ph); 150.1 (*s*, CHPh); 160.6 (*t*, *J*(P,C) = 11.1, ReC); 205.5 (*t*, *J*(P,C) = 6.9, CO); 206.6 (*t*, *J*(P,C) = 6.9, CO); 234.4 (*t*, *J*(P,C) = 2.5, $COC(CH_3)_3$). ^{31}P-NMR ($CDCl_3$): −20.0. MS: 582 (100, M^+), 554 (32, $[M - CO]^+$), 526 (88, $[M - 2\ CO]^+$), 450 (36, $[M - 2\ CO - PMe_3]^+$). Anal. calc. for $C_{21}H_{33}O_3P_2Re$ (581.6): C 43.37, H 5.72, Re 32.01; found: C 43.24, H 5.94, Re 31.37.

Bis(triethylphosphine)(dicarbonyl){η²(C,O)-[(E)-4,4-dimethyl-3-oxo-1-phenylpent-1-en-2-yl]}rhenium (**2e**). The reaction was carried out in Et_2O, the product extracted with toluene and filtered over *Celite*. Recrystallization from hexane/Et_2O afforded dark red crystals. Yield 90%. IR (hexane): 1914, 1837 (C≡O). ^{1}H-NMR (C_6D_6): 0.92 (*quint.*, *J*(H,H) = 7.3, *J*(P,H) = 14.5, 6 PCH_2CH_3); 1.22 (*s*, $(CH_3)_3C$); 1.64 (*m*, *J*(H,H) = 7.3, 6 PCH_2); 7.20–7.24, 7.36–7.43, 8.12–8.16 (*m*, Ph); 9.17 (*t*, *J*(P,H) = 2.1, =CH). ^{13}C-NMR (C_6D_6): 7.5 (*s*, $(CH_3CH_2)_3P$); 18.6 (*t*, *J*(P,C) = 13.5, $(CH_3CH_2)_3P$); 28.7 (*s*, $(CH_3)_3C$); 46.4 (*s*, $(CH_3)_3C$); 128.7, 128.9, 129.2, 141.5 (*s*, Ph), 150.5 (*s*, CHPh); 160.9 (*t*, *J*(P,C) = 10.4, ReC); 206.1 (*t*, *J*(P,C) = 7.5, CO); 206.6 (*t*, *J*(P,C) = 7.6, CO); 232.5 (*t*, *J*(P,C) = 2.5, $COC(CH_3)_3$). ^{31}P-NMR (C_6D_6): 9.9. MS: 666 (88, M^+), 638 (100, $[M - CO]^+$), 608 (22, $[M - CO - 2\ CH_3]^+$), 580 (8, $[M - 2\ CO - 2\ CH_3]^+$), 520 (38, $[M - CO - PEt_3]^+$), 490 (30, $[M - CO - 2\ CH_3 - PEt_3]^+$). Anal. calc. for $C_{27}H_{45}O_3P_2Re$ (666.8): C 48.71, H 6.81, Re 27.97; found: C 49.00, H 6.73, Re 27.23.

Synthesis of $\{Re(t\text{-}BuCO)(CO)_3[(i\text{-}PrO)_3]_2\}_n$ (**5b** or **6b**, $n = 1$ or 2, resp.). A soln. of **1b** (1.4 mmol) in THF (150 ml) was treated with *t*-BuLi (1 ml 1.4 mmol) at −80°. The mixture was allowed to warm up to r.t. and then evaporated to dryness. The residue was extracted with Et_2O and filtrated over *Celite*. After removing the solvent, the product was extracted with hexane. A white precipitate was formed immediately. The suspension was again filtered over *Celite*. The extraction was repeated with Et_2O. Evaporation of the solvent *in vacuo* afforded a white microcrystalline solid of **5b** or **6b**. IR (Et_2O): 1936, 1889, 1853 (C≡O). ^{1}H-NMR ((D$_{10}$)ether): 1.10 (*s*, $(CH_3)_3C$); 1.27 (*d*, J(H,H) = 6.3, 3 $(CH_3)_2CH$); 1.30 (*d*, J(H,H) = 7.1, 3 $(CH_3)_2CH$); 4.85 (*m*, J(H,H) = 6.3, J(H,H) = 7.1, 6 $(CH_3)_2CH$). ^{13}C-NMR ((D$_{10}$)ether): 24.7 (*s*, $(CH_3)_2CH$); 28.5 (*s*, $(CH_3)_2C$); 58.9 (*s*, $(CH_3)_3C$); 69.7 (*s*, $(CH_3)_2CH$); 187.3 (*t*, J(P,C) = 8.5, CO); 199.8 (*t*, J(P,C) = 9.0, CO); 305.6 (*t*, J(P,C) = 13.4, ReC). ^{31}P-NMR ((D$_{10}$)ether): 134.5. MS (M^+ assumed to be related to **5b**): 745 (28, M^+), 687 (100, $[M - 2\ CH_3 - CO]^+$), 659 (4, $[M - 2\ CH_3 - 2\ CO]^+$), 629 (6, $[M - 4\ CH_3 - 2\ CO]^+$).

Synthesis of Bis(phosphorus donor)(tert-*butylcarbonyl)(tricarbonyl)rhenium* (L = (i-PrO)$_3$P, **10b**; L = Et_3P, **10e**). A soln. of **1b** (1 g, 1.4 mmol; **1e**, 0.5 g, 0.93 mmol) in hexane (200 ml; 100 ml) was treated at −80° with *t*-BuLi (1 ml, 1.4 mmol; 0.7 ml, 0.98 mmol) and allowed to warm up to r.t. The mixture was then flushed with CO during 30 min. The solvent was evaporated *in vacuo* and the product extracted with hexane. Recrystallization from hexane gave yellow crystals **10b**. Yield 90% (**10e**: 80%).

Bis(triisopropoxyphosphine)(tert-*butylcarbonyl)(tricarbonyl)rhenium* (**10b**). IR (hexane): 2052, 1956, 1928, 1909 (C≡O). ^{1}H-NMR (C_6D_6): 1.24 (*d*, J(H,H) = 6.0, 6 $(CH_3)_2CH$); 1.42 (*s*, $(CH_3)_3C$); 4.71 (*m*, J(H,H) = 6.0, 6 POCH). ^{13}C-NMR (C_6D_6): 23.8 (*s*, $OCH(CH_3)_2$); 27.9 (*s*, $(CH_3)_3C$); 58.5 (*s*, $(CH_3)_3C$); 69.8 (*s*, $OCH(CH_3)_2$); 193.6 (*t*, J(P,C) = 8.9, CO); 193.6 (*t*, J(P,C) = 13.6, CO); 270.3 (*t*, J(P,C) = 14.4, ReC). ^{31}P-NMR (C_6D_6): 116.8. MS: 773 (14, M^+), 715 (100, $[M - 2\ CH_3 - CO]^+$), 687 (20, $[M - 2\ CH_3 - 2\ CO]^+$), 657 (22 $[M - 4\ CH_3 - 2\ CO]^+$), 629 (6, $[M - 4CH_3 - 3CO]^+$).

Bis(triethylphosphine)(tert-*butylcarbonyl)(tricarbonyl)rhenium* (**10e**). IR (hexane): 2033, 1927, 1899 (C≡O). ^{1}H-NMR (C_6D_6): 0.88 (*quint.*, J(H,H) = 7.6, J(P,H) = 15.3, 6 PCH_2CH_3); 1.17 (*s*, $(CH_3)_3C$); 1.71 (*m*, J(H,H) = 7.6, J(P,H) = 7.6, 6 PCH_2). ^{13}C-NMR (C_6D_6): 7.5 (*s*, $(CH_3CH_2)_3P$); 21.4 (*t*, J(P,C) = 14.7, $(CH_3CH_2)_3P$); 28.1 (*s*, $(CH_3)_3C$); 57.8 (*s*, $(CH_3)_3C$); 195.3 (*t*, J(P,C) = 7.1, CO); 196.9 (*t*, J(P,C) = 9.4, CO); 275.3 (*t*, J(P,C) = 10.3, ReC). ^{31}P-NMR (C_6D_6): −6.4. MS: 593 (42, M^+), 563 (2, $[M - C_2H_6]^+$), 535 (38, $[M - C_2H_6 - CO]^+$), 507 (18 $[M - C_2H_6 - 2\ CO]^+$), 475 (26, $[M - PEt_3]^+$), 445 (4, $[M - CO - C_2H_6 - PEt_3]^+$).

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