

59. Synthesis and Structure of η^4 -Enone Complexes of Ruthenium(0)

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A variety of $[\text{Ru}(\text{CO})_2\text{L}(\eta^4\text{-enone})]$ complexes (L = phosphines, phosphites, and arsines, enone = (*E*)-4-phenylbut-3-en-2-one) have been synthesized. ^1H -, ^{13}C -, and ^{31}P -NMR spectra are reported and the X-ray structures of two Ru complexes with L = Ph_3P (**7**), Et_3P (**10**) and one Fe complex with L = Ph_3P (**14**) are presented. All three compounds crystallize in the same monoclinic space group $P2_1/n$ with $a = 10.575(2)$ Å, $b = 9.213(2)$ Å, and $c = 27.608(5)$ Å, $\beta = 100.04(2)^\circ$, $Z = 4$ for **7**, $a = 10.276(3)$ Å, $b = 12.935(3)$ Å, and $c = 14.854(2)$ Å, $\beta = 96.96(2)^\circ$, $Z = 4$ for **10**, and $a = 10.492(2)$ Å, $b = 9.232(3)$ Å, and $c = 27.129(3)$ Å, $\beta = 98.67(2)^\circ$, $Z = 4$ for **14**. The structures of the Ru complexes are compared with the Fe analogues. In the case of M = Ru and L = $(\text{EtO})_3\text{P}$, $(\text{MeO})_3\text{P}$, and $(i\text{-PrO})_3\text{P}$ (**9**, **11**, and **13**, respectively) stereoisomers could be detected by ^{31}P -NMR at room temperature, which arise from rotation at the coordinated metal centre.

Introduction. – $[\text{Fe}(\text{CO})_2\text{L}(\eta^4\text{-enone})]$ complexes are known transfer reagents, since they are a convenient source of the $\text{Fe}(\text{CO})_2\text{L}$ moiety (L = CO, phosphines, and phosphites) [1]. The $\text{Fe}(\text{CO})_2\text{L}$ group can be transferred to another diene ligand under very mild conditions, which is useful in the case of thermal or photochemical instability of the diene ligand [1] [2]. These transfer reagents were also used to trap unstable products [3] and for kinetic resolution of non-functionalized $[\text{Fe}(\text{CO})_3(\eta^4\text{-diene})]$ complexes [4] [5]. For the synthesis of $[\text{Fe}(\text{CO})_3(\eta^4\text{-enone})]$ complexes, previous methods included either thermal reaction by heating the enone and $[\text{Fe}_2(\text{CO})_9]$ in toluene at $70^\circ\text{--}80^\circ$ [6] or irradiation of the enone and $\text{Fe}(\text{CO})_5$ in benzene [7]. The latter method usually yielded a mixture of the η^2 - and η^4 -coordinated compounds. Monosubstitution with L = phosphines or phosphites is best achieved by treating the tricarbonyl complex with trimethylamine oxide in a combination with a ligand L in MeCN [8] or directly by irradiation of $\text{Fe}(\text{CO})_4\text{L}$ (L = phosphines, phosphites) and the corresponding enone in benzene [2].

To our knowledge, attempts to synthesize η^4 -enone complexes of Ru have failed so far. $[\text{Ru}_3(\text{CO})_{12}]$ reacts in a complex manner with many dienes and enones to give, in addition to expected mononuclear products, triruthenium clusters and products resulting from H abstraction, see *e.g.* [9] [10]. Different methods for the complexation of diolefins with the $\text{Ru}(\text{CO})_3$ moiety were previously reported. The direct complexation of buta-1,3-diene derivatives was achieved by heating the ligand together with $[\text{Ru}_3(\text{CO})_{12}]$ in benzene. The best results in terms of yields were found with 1,4- and 2,3-disubstituted buta-1,3-diene ligands [11] [12]. It was also shown that amine oxides can promote complexation of the $\text{Fe}(\text{CO})_3$ group to dienes [13]. This method was used to synthesize tricarbonyl-[methyl (2*E*,4*E*)-hexa-2,4-dienoate]ruthenium [14]. Complexation of olefins and α,β -unsaturated carbonyl compounds to yield η^2 -complexes of Ru was also reported in the

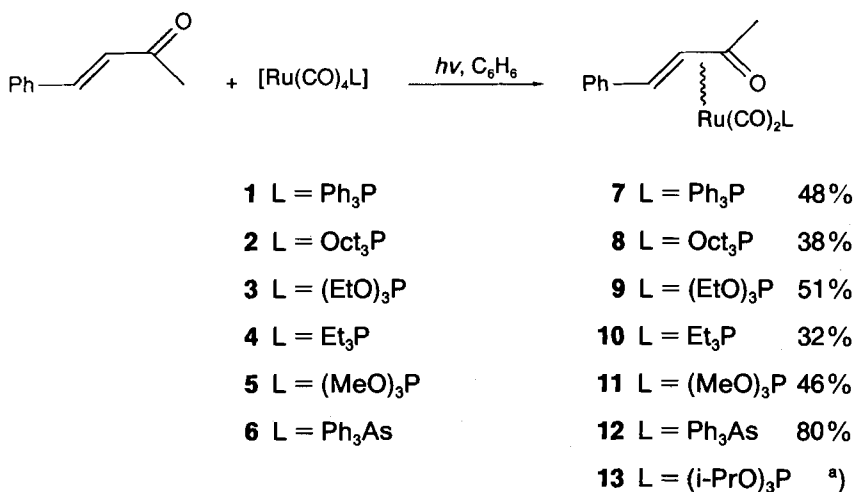
literature [15–17]. Several tricarbonyl complexes of Ru were synthesized by using $[\text{Ru}(\text{CO})_3(\text{cycloocta-1,5-diene})]$ as donating complex [12] [14]. However, all these methods failed, when (*E*)-4-phenylbut-3-en-2-one was used as the ligand [18]. In view of these facts, we have investigated a pathway for the synthesis of several new synthons of the type of $[\text{Ru}(\text{CO})_2\text{L}\{\eta^4\text{-(E)-4-phenylbut-3-en-2-one}\}]$, and their structures are compared with the corresponding Fe complexes. The new synthons are characterized by multinuclear NMR data. A detailed NMR study concerning possible rotamers, detectable at room temperature, is also reported.

Results and Discussion. – 1. *Syntheses.* In a previous paper, we have presented the synthesis of four optically active $[\text{Ru}(\text{CO})_2\text{L}(\eta^4\text{-enone})]$ complexes [19]. For their synthesis, we have envisaged a method, used before to achieve complexation of enones with the $\text{Fe}(\text{CO})_2\text{L}$ group. As already mentioned, irradiation of $[\text{Fe}(\text{CO})_4\text{L}]$ in benzene together with an excess of enone is quite an efficient method [2]. We have now reacted several $[\text{Ru}(\text{CO})_4\text{L}]$ complexes with (*E*)-4-phenylbut-3-en-2-one by irradiating a benzene solution of the two compounds with a high-pressure Hg lamp for several hours. The reaction was monitored by TLC and, on disappearance of the starting material ($[\text{Ru}(\text{CO})_4\text{L}]$), workup as described in the *Exper. Part* gave the desired products. Irradiation time depends on the ligand L in the starting complex and varies from 7 to 22 h. Yields for these reactions range from 38 to 80% (*Scheme 1*).

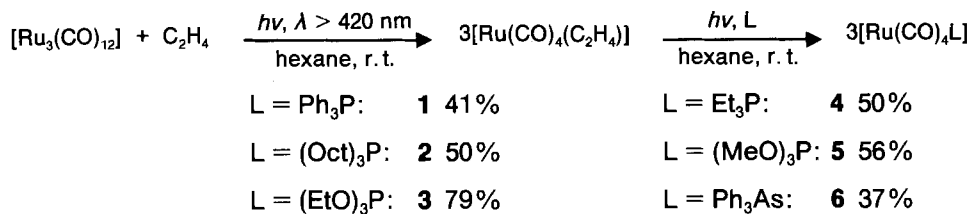
Most of the starting complexes 1–6 are known and described in the literature [20]. They can easily be prepared *in situ* by reacting L with $[\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)]$, which is generated in hexane solution by photolysis of $[\text{Ru}_3(\text{CO})_{12}]$ in the presence of ethylene [21]. The pure compounds 1–6 were obtained in yields ranging from 37–79% (based on Ru-atoms) (*Scheme 2*).

All attempts to synthesize $[\text{Ru}(\text{CO})_3\{\eta^4\text{-(E)-4-phenylbut-3-en-2-one}\}]$ failed: neither the procedure of *Grevels et al.* [16] nor that of *Johnson et al.* [21] of replacing ethylene in

Scheme 1


 a) See *Exper. Part*

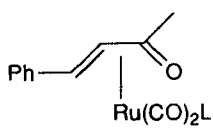
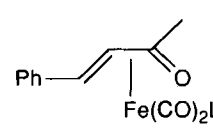
Scheme 2



[Ru(CO)₄(η²-ethylene)] by the heterodiene followed by decarbonylation gave the expected products. Even the attempt to displace Ph₃P in **7** by CO, as reported for similar complexes, did not give the desired products [22] [23]. All of these reactions resulted in the decomposition of the starting material. The Fe complexes [Fe(CO)₂L{η⁴-(*E*)-4-phenylbut-3-en-2-one}] **14–20**, corresponding to the Ru complexes **7–13**, were synthesized according to literature procedures [7] [8], for characterization see [2] [8] [24–26] and references therein. To our knowledge, the Oct₃P and (*i*-PrO)₃P complexes **15** and **20**, respectively, have not yet been described in the literature. Their spectroscopic data are given in the *Exper. Part*.

2. *Structure*. The structures of the new Ru synthons were confirmed by IR, ¹³C-, ³¹P-, and ¹H-NMR spectroscopy and in two cases determined by X-ray diffraction. The CO stretching frequencies of our dicarbonylruthenium complexes are higher than those of the corresponding Fe complexes. This could be explained by a smaller back-bonding in the case of Ru (*Table 1*). This tendency has been observed previously for compounds of the type of [M(CO)₂L(η⁴-diene)] (M = Fe and Ru) [27].

Table 1. CO Stretching Frequencies of [Ru(CO)₂L(η⁴-enone)] and [Fe(CO)₂L(η⁴-enone)] Complexes (cm⁻¹, CH₂Cl₂)

|  | | |  | | |
|---|-----------|------------|---|------------|--|
| | | | | | |
| L = Ph ₃ P | 7 | 2020, 1955 | 14 | 1995, 1935 | |
| L = Oct ₃ P | 8 | 2000, 1940 | 15 | 1990, 1930 | |
| L = (EtO) ₃ P | 9 | 2030, 1960 | 16 | 2005, 1945 | |
| L = Et ₃ P | 10 | 2010, 1940 | 17 | 1990, 1930 | |
| L = (MeO) ₃ P | 11 | 2030, 1960 | 18 | 2005, 1945 | |
| L = Ph ₃ As | 12 | 2020, 1950 | 19 | 1995, 1935 | |
| L = (<i>i</i> -PrO) ₃ P | 13 | 2020, 1960 | 20 | 2000, 1940 | |

The structures of **7** and **10** were determined by X-ray diffraction and compared with those of **14** and **17**. The two iron complexes are already described in the literature and have now been synthesized by CO displacement with L (L = Ph₃P, Et₃P) [2] [24], according to the procedure of *Adams et al.* [8]. *Tables 2* and *3* list the crystallographic data, selected bond distances, and bond angles. The molecular structures are given in *Figs. 1* and *2*. Since **7** and **14** are virtually isostructural, only the structures of **7** and **10** are illustrated.

Table 2. Data Collection and Structure Refinement Parameters

| | 7 | 10 | 14 |
|---|--|--|--|
| Crystallized from | hexane/Et ₂ O | hexane/Et ₂ O | hexane/Et ₂ O |
| Molecular formula | C ₃₀ H ₂₅ O ₃ PRu | C ₁₈ H ₂₅ O ₃ PRu | C ₃₀ H ₂₅ O ₃ PFe |
| Formula weight | 565.50 | 421.37 | 520.34 |
| Crystal color | yellow | yellow | orange |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>n</i> |
| <i>Unit Cell Parameters</i> | | | |
| No. of reflections refined | 21 | 24 | 25 |
| Angle range | 30° < 2θ < 32° | 38° < 2θ < 40° | 29° < 2θ < 36° |
| <i>a</i> [Å] | 10.575(2) | 10.276(3) | 10.492(2) |
| <i>b</i> [Å] | 9.213(2) | 12.935(3) | 9.232(3) |
| <i>c</i> [Å] | 27.608(5) | 14.854(2) | 27.129(3) |
| β [°] | 100.04(2) | 96.96(2) | 98.67(2) |
| <i>V</i> [Å ³] | 2648.6(9) | 1959.9(7) | 2598(1) |
| <i>Z</i> | 4 | 4 | 4 |
| <i>D</i> _x [g cm ⁻³] | 1.418 | 1.428 | 1.330 |
| Linear absorption coeff. [cm ⁻¹] | 6.658 | 8.737 | 6.668 |
| <i>Data Collection</i> | | | |
| <i>T</i> [K] | 297 | 173 | 294 |
| 2θ _{max} [°] | 55 | 55 | 50 |
| Reflections collected | 7567 | 4983 | 5842 |
| Unique reflections | 6052 | 4525 | 4588 |
| <i>R</i> _{int} | 0.036 | 0.018 | 0.045 |
| Max. and min. absorption correction | 1.097, 0.828 | 1.085, 0.913 | 1.157, 0.798 |
| <i>Refinement</i> | | | |
| Reflections observed (<i>I</i> > 3σ(<i>I</i>)) | 3759 | 4076 | 2508 |
| Least squares parameters | 416 | 309 | 405 |
| <i>R</i> , <i>wR</i> | 0.0343, 0.0351 | 0.0206, 0.0240 | 0.0421, 0.0397 |
| Goodness of fit <i>s</i> | 1.247 | 1.952 | 1.704 |
| Final <i>A</i> _{max} /σ | 0.0002 | 0.0002 | 0.0002 |
| <i>Δρ</i> (max) [e · Å ⁻³] | 0.38, -0.33 | 0.33, -0.47 | 0.33, -0.26 |

Table 3. Selected Bond Lengths [Å] and Bond Angles [°] of the Ru Complexes 7 and 10, and of the Fe Complex 14

| | 7 | 10 | 14 | 7 | 10 | 14 | |
|------------|-----------|-----------|----------|----------------|----------|-----------|----------|
| M–O(1) | 2.163(3) | 2.155(1) | 2.036(3) | P–M–O(1) | 98.16(7) | 98.35(4) | 95.1(1) |
| M–C(2) | 2.206(4) | 2.206(2) | 2.077(5) | P–M–C(2) | 132.1(1) | 132.42(5) | 131.7(1) |
| M–C(3) | 2.172(4) | 2.194(2) | 2.050(5) | P–M–C(3) | 135.3(1) | 133.63(6) | 135.6(2) |
| M–C(4) | 2.209(3) | 2.204(2) | 2.129(5) | P–M–C(4) | 99.48(9) | 97.40(5) | 98.2(1) |
| M–C(11) | 1.913(4) | 1.910(2) | 1.790(5) | M–C(2)–O(1) | 70.8(2) | 70.28(9) | 69.7(3) |
| M–C(12) | 1.840(4) | 1.847(2) | 1.750(5) | M–C(3)–C(2) | 72.5(2) | 71.8(1) | 71.2(3) |
| M–P | 2.3753(9) | 2.3387(6) | 2.264(1) | M–C(3)–C(4) | 72.4(2) | 71.4(1) | 73.2(3) |
| O(1)–C(2) | 1.306(5) | 1.320(2) | 1.314(6) | O(1)–C(2)–C(3) | 116.1(3) | 115.6(2) | 114.8(5) |
| C(2)–C(3) | 1.413(6) | 1.412(2) | 1.403(7) | C(2)–C(3)–C(4) | 117.9(4) | 117.2(2) | 118.2(5) |
| C(3)–C(4) | 1.422(5) | 1.432(3) | 1.417(7) | C(4)–M–C(12) | 95.0(1) | 99.21(8) | 92.6(2) |
| C(11)–O(2) | 1.133(6) | 1.146(2) | 1.140(7) | O(1)–M–C(11) | 95.8(1) | 92.91(7) | 94.4(2) |
| C(11)–O(3) | 1.152(5) | 1.153(2) | 1.143(6) | C(11)–M–P | 101.1(1) | 97.65(6) | 103.0(2) |
| C(1)–C(2) | 1.503(8) | 1.500(3) | 1.490(9) | C(12)–M–P | 94.9(1) | 92.24(6) | 97.2(2) |

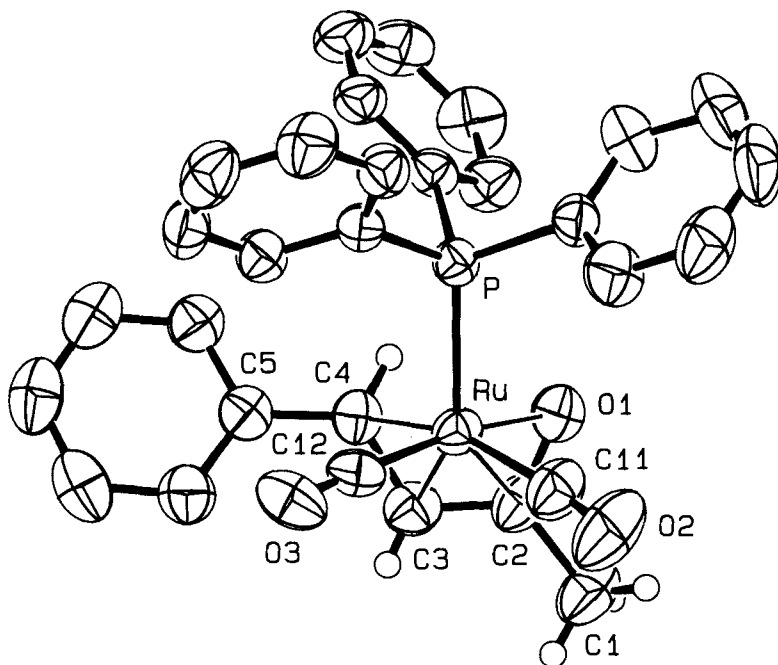


Fig. 1. Molecular structure of $[Ru(CO)_2(Ph_3P)\{(E)\text{-}4\text{-phenylbut-3-en-2-one}\}]$ (7)

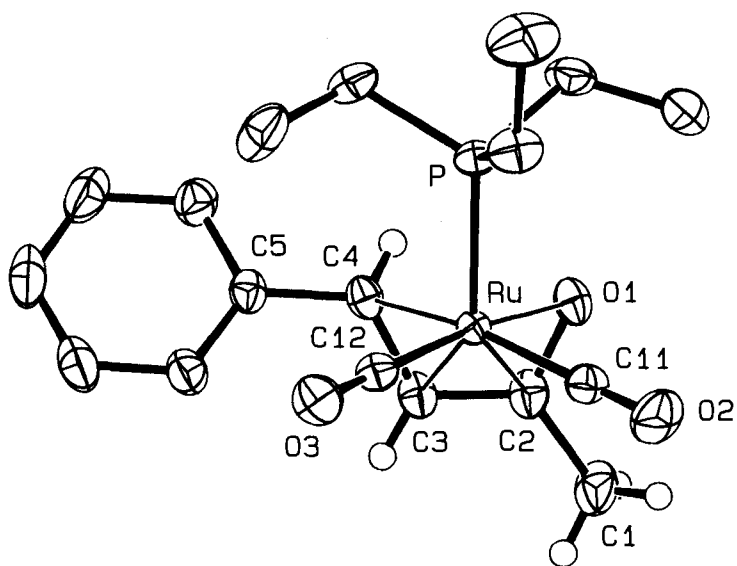
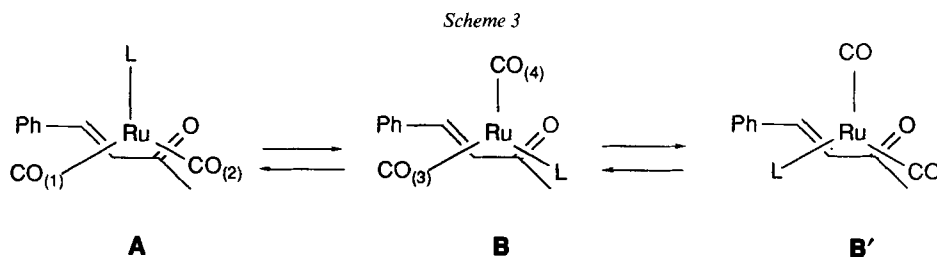


Fig. 2. Molecular structure of $[Ru(CO)_2(Et_3P)\{(E)\text{-}4\text{-phenylbut-3-en-2-one}\}]$ (10)

The crystal structure of **17** is already published in [24]. Compounds **7**, **10**, and **14** were crystallized from hexane/Et₂O at -20° . The coordination geometry of the metal atom is essentially the same for the four complexes and can be described as distorted square-pyramidal, where the base is defined by the CO ligands and the centres of the heterodiene double bonds. The P ligand is in the apical site. All the M–C-, M–O-, and M–P-bond lengths in general are longer in the case of the Ru complexes. This is in accordance with a smaller back donation as mentioned before. The C–C- and C–O-bond lengths of the heterodiene ligand are only slightly shorter for the Fe complexes **14** and **17**. Comparison of the bond angles does not show any essentially differences.

In solution and at low temperature, three rotamers **A**, **B**, and **B'** have to be considered which interconvert *via* formal enone rotation relative to the Ru(CO)₂L moiety (Scheme 3). Rotamers **A**, **B**, and **B'** should be observable by low-temperature ³¹P-NMR spectroscopy, as previously shown in the case of (η^4 -diene)iron complexes [8] [28].



Crystal-structure determinations of [Fe(CO)₂L{(E)-4-phenylbut-3-en-2-one}] (L = Et₃P, Ph₂PMe) [24] and [Fe(CO)₂(Ph₃P){(E)-3-phenylprop-2-enal}] [29] showed, that in the solid state the phosphine ligand is also in the apical position (rotamer **A**). A low-temperature NMR analysis of **14** and related compounds was reported by *Howell et al.* [30]. A room-temperature ³¹P-NMR spectrum of **14** consisted of a single peak, that showed splitting into a major and a minor signal upon cooling down to -70° . *Howell et al.* assigned the major resonance to the isomeric structure **A** and the minor resonance to the basal isomer **B**. The absence of the third rotamer **B'** was attributed to the difficulty of removing the best π -acceptor CO ligand from the position *trans* to the oxo group [31]. In the case of (alkoxyphosphine)ruthenium complexes [Ru(CO)₂L{(E)-4-phenylbut-3-en-2-one}] (L = (EtO)₃P, **9**; L = (MeO)₃P, **11**, and L = (i-PrO)₃P, **13**), ³¹P-NMR spectra show, at room temperature, two resonances which broaden and coalesce to a single line upon heating to 60° (Fig. 3). The ratios of the major and the minor signals are 100:8 for **9** and 100:6 for **11** and for **13**. Because of the similar ¹³C-NMR pattern of the CO resonances of the major isomer in **9**, **11**, and **13** and the CO resonances of **7** and **10** (all of the complexes show a *doublet* at lower field and a *singlet* at higher field) and by analogy to **14**, we also attribute the major signal to the conformation **A**. Unfortunately, we were not able to crystallize compounds **9**, **11**, and **13**, and thus a proof for **A** being also the solid-state structure is still missing. Fig. 4b shows a ¹³C,³¹P-correlation experiment at 285 K, which clearly correlates the ³¹P signals of the two rotamers of **11** with the corresponding ¹³C shifts of the CO groups of each rotamer. The F₂ axis shows the ³¹P-decoupled ¹³C-NMR

spectrum with the two CO shifts of the main isomer at 201.0 ppm (*d*, $J(\text{P},\text{C}) = 18$ Hz, CO(1)) and 196.0 ppm (*s*, CO(2)), and the two smaller signals of the minor rotamer at 201.7 ppm (*s*, CO(4)) and 200.8 ppm (*d*, $J(\text{P},\text{C}) = 18$ Hz, CO(3)), see also *Fig. 4a*. The F_1 axis shows the ^{31}P resonances of the major (157.1 ppm) and the minor isomer (151.0 ppm). Only one of the two minor ^{13}C signals (CO(3)) correlates with the minor ^{31}P signal. The second correlation is not observable because of low signal intensity and a very small P,C coupling. The large difference between the ^{31}P , ^{13}C -coupling constants of the two basal CO groups with the apical P ligand was also reported for the Fe complex **14** [30].

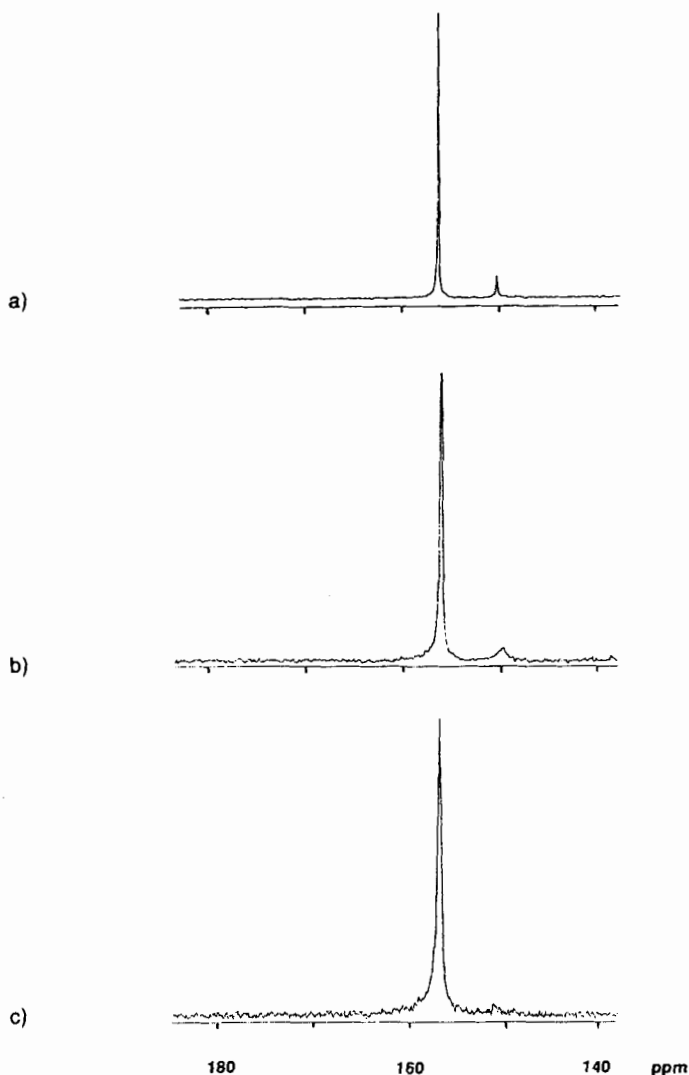


Fig. 3. ^{31}P -NMR Spectra of $[\text{Ru}(\text{CO})_2(\text{MeO})_3\text{P}]\{(\text{E})\text{-4-phenylbut-3-en-2-one}\}$ (**11**) (80.7 MHz, C_6D_6) at variable temperature. a) 25°, b) 45°, and c) 60°.

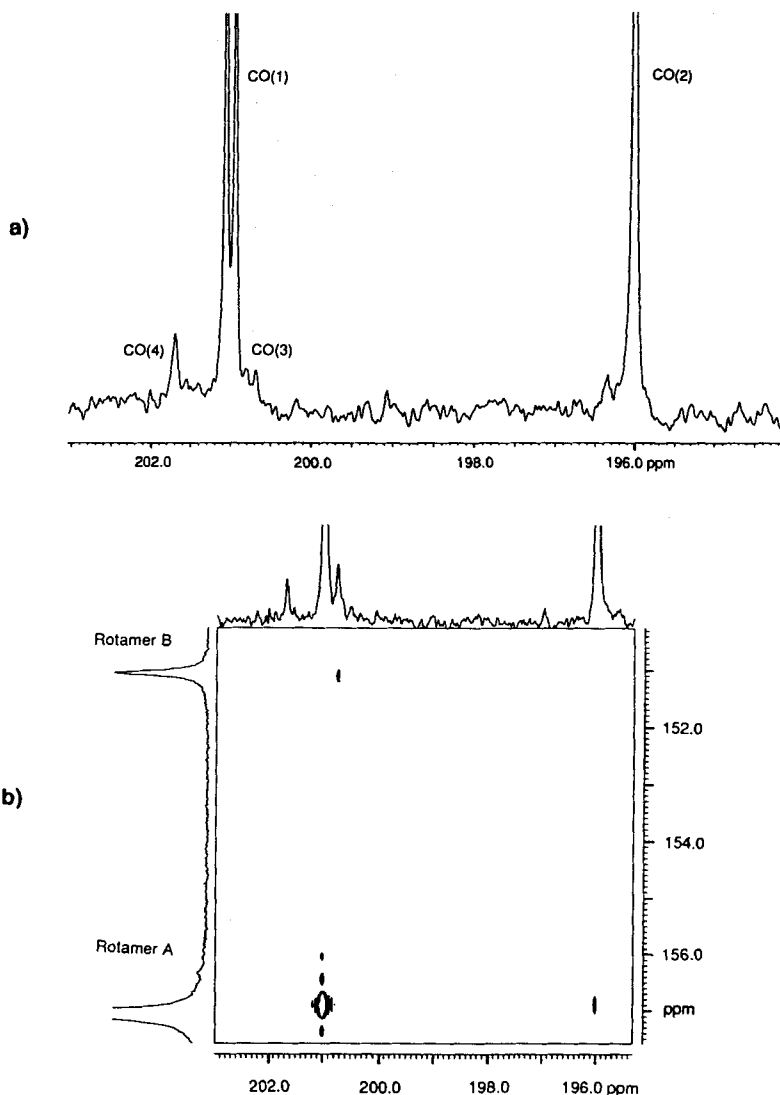


Fig. 4. a) ^{31}P -Coupled ^{13}C -NMR spectrum of $[\text{Ru}(\text{CO})_2(\text{MeO})_3\text{P}\{(E)\text{-}4\text{-phenylbut-3-en-2-one}\}]$ (**11**). b) ^{13}C , ^{31}P Correlation experiment on **11**, ^{31}P decoupled in F_2 . Both spectra were recorded at 285 K in C_6D_6 (242 MHz).

By comparing the M–CO bond lengths in **7**, **10**, and **14**, we have tried to give an absolute assignment to the CO resonances. As already described for similar complexes [30] [32], we have also found that in these compounds the M–CO bonds are longer in the case of the CO *cis* to the oxo group. *Howell et al.* [30] attributed this behavior to a smaller π -back-donation and assigned the up-field signals to the CO *cis* to the oxo group ($\delta(\text{C}(11)) < \delta(\text{C}(12))$, see *Figs. 1* and *2*).

Fig. 4a shows the ^{31}P -coupled ^{13}C -NMR spectrum of **11**. With the assumption that the replacement of Fe by Ru is expected to have no influence on the relative positions of the CO resonances, we have now tried to assign the minor rotamer either to structure **B** or **B'**. The two CO resonances of the minor rotamer (CO(3) and CO(4)) appear in the region of the doublet of the major isomer, i.e. in the region of the CO *trans* to the oxo group (CO(1); Fig. 4a). According to [30], the CO in the apical site is usually the most deshielded of the CO ligands in the three possible positions. This leads to structure **B** for the minor rotamer appearing in the ^{31}P -NMR spectrum of **9**, **11**, and **13**. This assignment is also in accordance with observations made by *Al-Ohaly et al.* [33]. They have shown that in $[\text{Ru}(\text{butadiene})((\text{MeO})_3\text{P})_2(\text{Ph}_3\text{P})]$, which exists as a mixture of two rotamers, the P,P coupling constants are larger, when the two P-atoms are in basal position ($J((\text{MeO})_3\text{P}(\text{basal}) - \text{Ph}_3\text{P}(\text{basal})) > J((\text{MeO})_3\text{P}(\text{axial}) - \text{Ph}_3\text{P}(\text{basal}))$). In our case then, the coupled CO signal of the minor rotamer at 200.8 ppm is the CO *trans* to the oxo group. For the CO in the apical site no coupling is resolved.

The ^{31}P -NMR spectrum of $[\text{Fe}(\text{CO})_2(\text{MeO})_3\text{P}\{(E)\text{-4-phenylbut-3-en-2-one}\}]$ (**18**) at room temperature shows one absorption at 176.0 ppm (121.0 MHz, CDCl_3) which, on cooling to -40° , also resolves into two signals showing a new minor absorption at 174.0 ppm. The only difference to the Ru analogue **11** is the lower coalescence temperature. A similar behavior has been observed in a low-temperature NMR study concerning rotamers in $[\text{M}(\text{CO})\text{L}^1\text{L}^2]$ complexes of methyl (2*E*,4*E*)-hexa-2,4-dienoate ($\text{M} = \text{Ru, Fe}$; $\text{L}^1, \text{L}^2 = \text{phosphines and phosphites}$). In the case of Ru, rotamers could already be detected at room temperature [27], whereas the Fe complexes show separate rotamer signals only at low temperature.

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Experimental Part

1. *Analytical Methods.* IR Spectra were recorded on a *Perkin-Elmer 298* spectrometer, ^1H -NMR spectra on a *Bruker AM-300* (300 MHz), and ^{13}C - and ^{31}P -NMR spectra on a *Varian XL-200* spectrometer (50 MHz and 80.7 MHz). Special NMR experiments were performed on a *Bruker AMX-600* spectrometer. $\delta(\text{H})$ and $\delta(\text{C})$ are reported relative to an internal standard (TMS), $\delta(\text{P})$ relative to 85% H_3PO_4 as an external standard. Spectra were recorded at 300 K if not indicated otherwise. Microanalyses of all crystalline compounds gave satisfactory results.

2. *X-Ray Crystallographic Study of 7, 10, and 14* (see also Tables 2 and 3). Intensity data were collected using a *Rigaku AFC5R* diffractometer (for **10** and **14**) and a *Nicolet R3* diffractometer (for **7**) with MoK_α radiation (graphite-monochromated, $\lambda = 0.71069 \text{ \AA}$). Three standard reflections were monitored throughout each data collection and remained stable. An empirical absorption correction was applied to each data set [34]. The structures were solved using SHELXS-86 [35] and refined using the TEXSAN program system [36]. For **7** and **10**, the structures were solved by *Patterson* methods which revealed the positions of the Ru-atom of **7** and the Ru- and P-atoms of **10**, the remaining non-H-atoms being located in a *Fourier* expansion of the *Patterson* solution. For **14**, the structure was solved by direct methods, which revealed the positions of all non-H-atoms. All non-H-atoms were refined anisotropically. All of the H-atoms were located in a difference-electron-density map, and, except for one Ph and the Me H-atoms in **14**, their positions were allowed to refine together with individual isotropic temp. factors. The remaining four H-atoms were replaced in geometrically calculated positions ($d(\text{C}-\text{H}) = 0.95 \text{ \AA}$) with only their temp. factors being refined.

3. *Syntheses.* The tetracarbonylruthenium complexes **1-6** were synthesized according to [21] and complexes **14** and **16-19** with the procedure given in [7] [8]. $[\text{Ru}_3(\text{CO})_{12}]$ was purchased from *Strem Chemicals*. Common solvents were distilled prior to use. All synthetic operations were carried out under inert atmosphere in dry, O_2 -free solvents. Chromatographic operations were performed on silica gel 60 (*Merck*) using hexane/ Et_2O as eluent.

General Procedure for the Synthesis of $[Ru(CO)_4L]$ Complexes (1–6). These complexes were synthesized according to the procedure of Chen and Poé [20a]. A suspension of 1 g (1.56 mmol) of $[Ru_3(CO)_{12}]$ in 150 ml of hexane was flushed with ethylene and then irradiated with a high-pressure Hg lamp, until the orange suspension turned into a colorless soln. (ca. 1 h). During irradiation, ethylene was bubbled through the soln. A sat. $NaNO_2$ soln. was used as a short-wave-lengths cutoff filter. The ligands L were then added (4.5 mmol), and the irradiation was carried on, until no further ethylene formation was observed. On completion of the reaction, the soln. was concentrated *in vacuo*, and the oily residue was then chromatographed using hexane/ Et_2O as eluent. Yields ranged from 30 to 60% (based on Ru-atoms).

General Procedure for the Synthesis of $[Ru(CO)_2L((E)-4\text{-phenylbut-3-en-2-one})]$ Complexes (7–12). A soln. of $[Ru(CO)_4L]$ (1.6 mmol) and benzylideneacetone (6.4 mmol) in 150 ml of benzene was irradiated with a high-pressure Hg-lamp (Philips HPK 125 W or Hanau 250 W). The reaction was monitored by TLC and, on disappearance of the starting material ($[Ru(CO)_4L]$), the soln. was filtered through *Celite* and the solvent removed under reduced pressure at 40°. The oily residue was chromatographed on silica gel using hexane/ Et_2O as eluent.

Procedure for the Synthesis of Dicarbonyl[O-4- η -((E)-4-phenylbut-3-en-2-one)](triisopropyl phosphite)ruthenium (13). Tetracarbonyl(triisopropyl phosphite)ruthenium was synthesized as described above for complexes 1–6. After 9 h, the soln. was filtered through *Celite* and the solvent removed under reduced pressure at r.t. Since the oily residue could not be further purified, it was dissolved in 150 ml of benzene and the enone was added (10 mmol). The soln. was again irradiated for 9 h. After filtration through *Celite* and removal of the solvent under reduced pressure at 40°, the residue was chromatographed on silica gel using hexane/ Et_2O 3:1 yielding 250 mg of a dark-red oily product.

Tetracarbonyl(trioctyl phosphine)ruthenium (2). Yield: 30%. Dark-red oil. IR (CH_2Cl_2): 3010–2860m, 2060m, 1970m, 1935s. 1H -NMR (300 MHz, C_6D_6): 1.59–1.24 (m, CH_2); 0.92 (t, $J(H,H) = 6.8$, CH_3). ^{13}C -NMR (50 MHz, C_6D_6): 205.4 (m, CO); 32.4–23.0 (m, CH_2); 14.3 (s, CH_3). ^{31}P -NMR (80.7 MHz, C_6D_6): 29.6 (s).

Dicarbonyl[O-4- η -((E)-4-phenylbut-3-en-2-one)](triphenylphosphine)ruthenium (7). Yield: 48%. Yellow crystals, decomposition point 150°. IR (CH_2Cl_2): 2020s, 1955s. 1H -NMR (300 MHz, C_6D_6): 7.45–6.77 (m, 20 H, Ph); 5.49 (dd, $J(H,H) = 8.0$, $J(P,H) = 3.7$, H–C(3)); 2.38 (d, $J(P,H) = 3.8$, H–C(1)); 2.29 (t, $J(H,H) = J(P,H) = 8.0$, H–C(4)). ^{13}C -NMR (50 MHz, $CDCl_3$): 201.2 (d, $J(P,C) = 10.2$, CO); 196.8 (s, CO); 141.1–124.5 (m, Ph, C(2)); 81.1 (s, C(3)); 58.3 (s, C(4)); 21.5 (d, $J(P,C) = 2$, C(1)). ^{31}P -NMR (80.7 MHz, $CDCl_3$): 37.3 (s).

Dicarbonyl[O-4- η -((E)-4-phenylbut-3-en-2-one)](trioctylphosphine)ruthenium (8). Yield: 38%. Brown oil. IR (CH_2Cl_2): 2930–2860m, 2000s, 1940s. 1H -NMR (300 MHz, C_6D_6): 7.45–6.93 (m, Ph); 5.35 (dd, $J(H,H) = 7.5$, $J(P,H) = 3.7$, H–C(3)); 2.54 (t, $J(H,H) = J(P,H) = 7.5$, H–C(4)); 2.40 (d, $J(P,H) = 3.4$, H–C(1)); 1.84–1.11 (m, CH_2); 0.92 (t, $J(H,H) = 6.6$, CH_3). ^{13}C -NMR (50 MHz, C_6D_6): 203.2 (d, $J(P,C) = 8$, CO); 198.8 (s, CO); 144.1 (d, $J(P,C) = 2$, C(2)); 142.4 (s, C(1) of Ph); 128.0, 125.7, 124.0 (s, Ph); 78.9 (s, C(3)); 52.6 (s, C(4)); 31.7–22.5 (m, CH_2); 20.9 (s, C(1)); 13.8 (s, CH_3). ^{31}P -NMR (80.7 MHz, C_6D_6): 21.1 (s).

Dicarbonyl[O-4- η -((E)-4-phenylbut-3-en-2-one)](triethyl phosphite)ruthenium (9). Yield: 40%. Yellow oil. IR (CH_2Cl_2): 2030s, 1960s. 1H -NMR (300 MHz, C_6D_6): 7.28–6.94 (m, Ph); 5.38 (m, H–C(3)); 3.99–3.77 (m, CH_2); 3.01 (t, $J(P,H) = J(H,H) = 8.5$, H–C(4)); 2.34 (d, $J(P,H) = 5.8$, H–C(1)); 1.04 (t, $J(H,H) = 7.1$, CH_3). ^{13}C -NMR (50 MHz, $CDCl_3$): 200.2 (d, $J(P,C) = 18$, CO); 194.9 (d, $J(P,C) = 2.5$, CO); 143.3–140.0 (m, C(2), C(1) of Ph); 128.0, 125.9, 124.4 (s, Ph); 79.3 (d, $J(P,C) = 2$, C(3)); 60.8 (d, $J(P,C) = 2$, CH_2); 51.7 (s, C(4)); 21.1 (d, $J(P,C) = 3$, C(1)); 16.0 (d, $J(P,C) = 7$, CH_3). ^{31}P -NMR (120.8 MHz, C_6D_6): 150.7 (s, major isomer); 145.0 (s, minor isomer).

Dicarbonyl[O-4- η -((E)-4-phenylbut-3-en-2-one)](triethylphosphine)ruthenium (10). Yield: 32%. Yellow oil. 1H -NMR (300 MHz, C_6D_6): 7.17–6.94 (m, Ph); 5.35 (dd, $J(H,H) = 7.4$, $J(P,H) = 3.7$, H–C(3)); 2.48 (t, $J(H,H) = J(P,H) = 7.4$, H–C(4)); 2.38 (d, $J(P,H) = 3.4$, H–C(1)); 1.52 (quint., $J(H,H) = J(P,H) = 7.4$, CH_2); 0.74 (dt, $J(P,H) = 16.4$, $J(H,H) = 7.4$, CH_3). ^{13}C -NMR (50 MHz, C_6D_6): 203.0 (d, $J(P,C) = 11$, CO); 198.6 (s, CO); 144.5 (s, C(2)); 142.8 (s, C(1) of Ph); 128.5, 126.2, 124.5 (s, Ph); 79.2 (d, $J(P,C) = 2$, C(3)); 52.7 (s, C(4)); 21.4 (d, $J(P,C) = 2$, C(1)); 19.8 (d, $J(P,C) = 25$, CH_2); 7.5 (d, $J(P,C) = 2$, CH_3). ^{31}P (80.7 MHz, C_6D_6): 28.7 (s).

Dicarbonyl[O-4- η -((E)-4-phenylbut-3-en-2-one)](trimethyl phosphite)ruthenium (11). Yield: 46%. Yellow oil. IR (CH_2Cl_2): 2950–2850w, 2030s, 1960s. 1H -NMR (300 MHz, C_6D_6): 7.19–6.93 (m, Ph); 5.37 (dd, $J(H,H) = 7.6$, $J(P,H) = 5.2$, H–C(3)); 3.29 (d, $J(P,H) = 12.5$, $P(OCH_3)$); 3.02 (t, $J(H,H) = J(P,H) = 7.6$, H–C(4)); 2.32 (d, $J(P,H) = 5.8$, H–C(1)). ^{13}C -NMR (50 MHz, C_6D_6): 201.0 (d, $J(P,C) = 18$, CO, major isomer); 196.0 (s, CO, major isomer); 201.7 (s, CO, minor isomer); 200.8 (d, $J(P,C) = 18$, minor isomer); 143.1 (d, $J(P,C) = 2$, C(2)); 142.6 (s, C(1) of Ph); 128.5–124.4 (m, Ph); 78.2 (d, $J(P,C) = 2.4$, C(3)); 51.1 (m, C(4), $P(OCH_3)$); 20.5 (d, $J(P,C) = 2.8$, C(1)). ^{31}P -NMR (120.8 MHz, C_6D_6): 156.3 (s, major isomer); 151.0 (s, minor isomer).

Dicarbonyl[O-4- η -((E)-4-phenylbut-3-en-2-one)](triphenylarsine)ruthenium (12). Yield: 80%. Yellow oily crystals. IR (CH_2Cl_2): 2020s, 1950s. 1H -NMR (300 MHz, C_6D_6): 7.40–6.95 (m, Ph); 5.53 (d, $J(H,H) = 8.1$,

H–C(3)); 2.64 (*d*, *J*(H,H) = 8.1, H–C(4)); 2.37 (*s*, H–C(1)). ¹³C-NMR (50 MHz, CDCl₃): 200.9 (*s*, CO); 197.0 (*s*, CO); 142.1–124.6 (*m*, Ph, C(2)); 80.7 (*s*, C(3)); 57.2 (*s*, C(4)); 21.6 (*s*, C(1)).

Dicarbonyl[O-4-η-(E)-4-phenylbut-3-en-2-one](triisopropyl phosphite)ruthenium (13). Yellow oil. IR (CH₂Cl₂): 2020*s*, 1960*s*. ¹H-NMR (300 MHz, C₆D₆): 7.28–6.95 (*m*, Ph); 5.31 (*m*, H–C(3)); 4.77–4.66 (*m*, CH); 2.99 (*t*, *J*(H,H) = *J*(P,H) = 7.8, H–C(4)); 2.34 (*d*, *J*(P,H) = 5.5, H–C(1)); 1.16 (*d*, *J*(H,H) = 6.1, CH₃). ¹³C-NMR (50 MHz, CDCl₃): 205.8–195.5 (*m*, CO); 143.3 (*d*, *J*(P,C) = 2, C(2)); 139.8 (*s*, C(1) of Ph); 127.9, 126.2, 124.3 (*s*, Ph); 79.5 (*s*, C(3)); 69.4 (*d*, *J*(P,C) = 3, CH); 51.8 (*s*, C(4)); 24.0 (*m*, CH₃); 21.2 (*d*, *J*(P,C) = 3, C(1)). ³¹P-NMR (80.7 MHz, C₆D₆): 146.5 (*s*, major isomer); 145.7 (*s*, minor isomer).

Dicarbonyl[O-4-η-(E)-4-phenylbut-3-en-2-one](trioctylphosphine)iron (15). Yellow oil. IR (CH₂Cl₂): 1990*s*, 1930*s*. ¹H-NMR (300 MHz, C₆D₆): 7.62–7.02 (*m*, Ph); 5.36 (*d*, *J*(H,H) = 8.1, H–C(3)); 2.57 (*m*, H–C(4)); 2.33 (*d*, *J*(P,H) = 1.9, H–C(1)); 1.90–1.24 (*m*, CH₂); 0.91 (*t*, *J*(H,H) = 6.2, CH₃). ¹³C-NMR (50 MHz, C₆D₆): 216.3 (*d*, *J*(P,C) = 14, CO); 210.7 (*s*, CO); 144.1 (*s*, C(2)); 139.5 (*s*, C(1) of Ph); 129.1, 129.0, 125.5 (*s*, Ph); 79.3 (*s*, C(3)); 58.2 (*d*, *J*(P,C) = 2, C(4)); 32.7–23.6 (*m*, CH₂); 27.7 (*d*, *J*(P,C) = 23, (CH₂P)); 21.9 (*s*, C(1)); 14.8 (*s*, CH₃). ³¹P-NMR (80.7 MHz, C₆D₆): 37.4 (*s*).

Dicarbonyl[O-4-η-(E)-4-phenyl-3-buten-2-one](triisopropyl phosphite)iron (20). Yellow oil. IR (CH₂Cl₂): 2005*s*, 1945*s*. ¹H-NMR (300 MHz, CDCl₃): 7.25–7.05 (*m*, Ph); 5.65 (*dd*, *J*(H,H) = 8.8, *J*(P,H) = 2.1, H–C(3)); 4.60 (*m*, H–C–O); 2.60 (*m*, H–C(4)); 2.49 (*d*, *J*(P,H) = 3.6, H–C(1)); 1.28 (*d*, *J*(H,H) = 6.1, CH₃); 1.24 (*d*, *J*(H,H) = 6.1, CH₃). ¹³C-NMR (50 MHz, C₆D₆): M–CO not observable; 141.8 (*d*, *J*(P,C) = 2, C(2)); 136.5 (*s*, C(1) of Ph); 128.1, 127.1, 125.2 (*s*, Ph); 77.9 (*s*, C(3)); 69.0 (*d*, *J*(P,C) = 4, C–O); 58.2 (*d*, *J*(P,C) = 2, C(4)); 23.9 (*m*, CH₃); 20.8 (*d*, *J*(P,C) = 2, C(1)). ³¹P-NMR (161.4 MHz, CDCl₃): 166.6 (*s*).

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