Formation of 18e⁻ and 16e⁻ Acyl(η^3-cyclooctenyl)rhodium(III) Complexes in the Reaction of Cationic (Cycloocta-1,5-diene)rhodium(I) Compounds with 2-(Diphenylphosphino)benzaldehyde

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The reaction of cationic diolefinic rhodium(I) complexes with 2-(diphenylphosphino)benzaldehyde (pCHO) was studied. $[Rh(cod)_2]ClO_4$ (cod = cycloocta-1,5-diene) reacted with pCHO to undergo the oxidative addition of one pCHO with (1,2,3-η)cyclooct-2-en-1-yl (η^3-C_8H_{13}) formation, and the coordination of a second pCHO molecule as (phosphino-κP)aldehyde-κO(σ-coordination) chelate to give the 18e⁻ acyl(allyl)rhodium(III) species $[Rh(\eta^3\text{-}C_8H_{13})(pCO)(pCHO)]ClO_4$ (see **1**). Complex **1** reacted with $[Rh(cod)(PR_3)_2]ClO_4$ (R = aryl) derivatives **3**–**6** to give stable pentacoordinated 16e⁻ acyl[(1,2,3-η)-cyclooct-2-en-1-yl]rhodium(III) species $[Rh(\eta^3\text{-}C_8H_{13})(pCO)(PR_3)]ClO_4$ **7**–**10**. The (1,2,3-η)-cyclooct-2-en-1-yl complexes contain *cis*-positioned P-atoms and were fully characterized by NMR, and the molecular structure of **1** was determined by X-ray crystal diffraction. The rhodium(III) complex **1** catalyzed the hydroformylation of hex-1-ene and produced 98% of aldehydes (n/iso = 2.6).

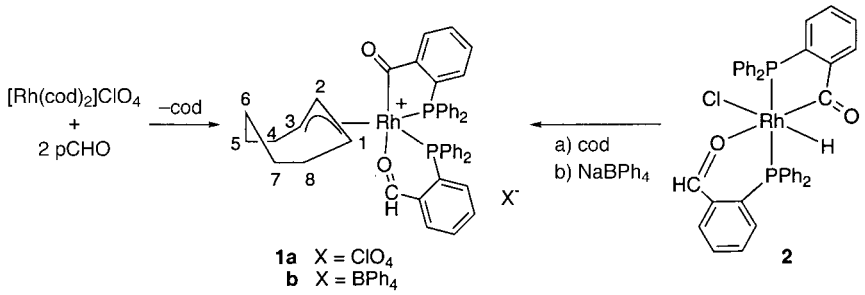
Introduction. – The activation of C–H bonds promoted by transition-metal complexes is an active area of research [1]. Cleavage of C–H bonds of aldehydes and promoted by Rh may lead to acylhydrido species [2]. When the aldehyde is close to a donor atom and chelates can be formed, the corresponding acylhydrido complexes are easily obtained [3–4], and some of them are active catalysts in the hydroacylation of olefins [4]. The 2-(diphenylphosphino)benzaldehyde (pCHO) has been used to add oxidatively to several late transition metals in low oxidation states [3][5–6], yielding *cis*-acylhydrido complexes that contain (phosphino-κP)acyl-κC chelates (pCO). Hydrido complexes containing cycloocta-1,5-diene may undergo insertion of the olefin into the M–H bond to afford (1,4,5-η)-cyclooct-4-en-1-yl ((1-σ-4,5-η^2)-C_8H_{13}) [7] or the corresponding π-allylic type (1,2,3-η^3)-C_8H_{13}) derivatives [8]. Also, [RhCl(penta-1,4-diene)]$_2$ has been reported to react with quinoline-8-carboxaldehyde (nCHO) to give an 18e⁻ acylallyl compound $[RhCl(\eta^3\text{-}1\text{-ethylallyl})(nCO)]_2$ *via* an acyl(hydrido)-diolefin intermediate [9]. In contrast, the diolefinic complex $[IrCl(cod)]_2$ reacts with pCHO to give the thermally unstable [IrH(pCO)Cl(cod)] that has been proposed as model intermediate in the hydroacylation of olefins [5a], and we have recently reported that $[RhCl(cod)]_2$ and [Rh(cod)(bdh)Cl] (cod = cycloocta-1,5-diene, bdh = biacetyldihydrazone) react with pCHO (Rh/pCHO 1:2) to give acylhydrido derivatives with displacement of cycloocta-1,5-diene [10].

We report now on the reaction of $[Rh(cod)_2ClO_4$ with pCHO (Rh/pCHO 1:2), which adds oxidatively to form a fully characterized 18e⁻ acyl[(1,2,3-η)-cyclooct-2-en-

1-yl]rhodium(III) derivative, which also contains a (phosphino-κP)aldehyde-κO chelate, *i.e.*, $[Rh(\eta^3\text{-}C_8H_{13})(pCO)(pCHO)]ClO_4$. Its reactivity with cationic $[Rh(cod)(PR_3)_2]ClO_4$ compounds to give 16e$^-$ acyl[(1,2,3-η)-cycloct-2-en-1-yl]rhodium(III) derivatives and the catalytic activity in hex-1-ene hydroformylation is also reported.

Results and Discussion. – $[Rh(cod)_2]ClO_4$ reacts with pCHO (Rh/pCHO 1:2) in CH_2Cl_2 to undergo the displacement of one cycloocta-1,5-diene ligand, the oxidative addition of one pCHO with concomitant η^3-cyclooctenyl (η^3-C_8H_{13}) formation, and the coordination of a second pCHO molecule as (phosphino-κP)aldehyde-κO (σ-coordination chelate) to give the 18e$^-$ species $[Rh(\eta^3\text{-}C_8H_{13})(pCO)(pCHO)]ClO_4$ **1a**, as shown in *Scheme 1*. Compound **1a** behaves as a 1:1 electrolyte in acetone solution [11]. The structure of **1a** was established by its ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra, ^{1}H,^{1}H-COSY and ^{13}C,^{1}H-correlation experiments, and mass spectra and confirmed by an X-ray crystal-diffraction study (see below).

Scheme 1



The ^{31}P{^{1}H}-NMR spectrum of **1a** shows 2 *dd* corresponding to an *AMX* pattern with $J(P,P) = 16$ Hz, which agrees with a *cis* arrangement of the P-atoms, and in the ^{13}C{^{1}H}-NMR spectrum, a *d* due to the coordinated acyl group of pCO is observed at *ca.* 218 ppm ($J(Rh,C) = 28$ Hz). The FAB-MS exhibits a molecular-ion peak at 791, a $[M - C_8H_{12}]^+$ peak at 683, and a $[M - C_8H_{12} - 2CO]^+$ peak at 627.

In the ^{1}H-NMR spectrum, the allyl group generates 3 *m* that integrate in a relative ratio of 1:1:1 in the expected range for η^3-cyclooctenyl complexes [8a][12]. The resonance at 4.75 (*t*) ppm can be assigned to the proton at position 2 and is only coupled to H–C(1) and H–C(3) as shown by the 2D-{^{1}H,^{1}H}-COSY spectrum. The identity of the coupling constants $J(1,2) = J(3,2) = 8.0$ Hz is in agreement with a *cis*-arrangement of the three H-atoms at the η^3-allyl moiety. The resonances at 4.41 (*m*) and 3.72 (*m*) are typical for H–C(1) and H–C(3), respectively, and their chemical shifts are different because they are *trans* to the P-atoms belonging to different chelate ligands. Selective irradiation of the P-atoms at their resonance frequency allows the identification of H–C(1) and H–C(3) being *trans* to pCO and pCHO, respectively. In the ^{13}C{^{1}H}-NMR spectrum, C(2) appears as a *d* at 113.6 ppm, and the magnetically inequivalent C(1) and C(3) at 90.1 and 80.2 ppm, respectively, show *dd*s due to coupling to Rh and to the corresponding *trans*-positioned P-atom. The coupling constants for both C-atoms are identical and are similar to those reported for the rhodium(I) complex, $[Rh(\eta^3\text{-}C_8H_{13})\{(-)diop\}]$ [13]. The assignments are confirmed by 2D-^{13}C,^{1}H correlation.

The formation of the allyl group can be explained assuming the initial oxidative addition of pCHO with formation of an acylhydrido rhodium(III) complex, which in the presence of an anion of low coordinating ability also contains a bonded diolefin. The insertion of a C=C bond into the Rh–H bond followed by the rearrangement of

the π-olefin/σ-alkyl ligand (1,4,5-η)-cyclooct-4-en-1-yl thus formed, gives the thermodynamically stable η^3-allyl derivative ((1,2,3-η)-cyclooct-2-en-1-yl ligand). This is confirmed by the reaction of [Rh(H)(Cl)(pCO)(pCHO)] **2** [10b] (prepared *in situ*) with cycloocta-1,5-diene in the presence of $NaBPh_4$, which yields **1b** (see *Scheme 1*). We believe that dissociation of the Cl ligand in **2** allows coordination of the diolefin and its transformation into cyclooctenyl.

Complex **1** contains also pCHO as a chelating phosphino aldehyde. pCHO has been reported to coordinate as chelate with the aldehyde portion bonded through the O-atom (σ-complex) in [$RuCl_2$(pCHO)$_2$] [5a] and $ReX(CO)_3$(pCHO)] [14] or through both the O- and C-atom (π-complex) in [$Co(C_5Me_5)$(pCHO)] [15]. Both σ- and π-bonding modes are well-known for aldehyde complexes of transition metals [16], though very few (aldehyde)rhodium derivatives have been reported [17]. The NMR spectra of **1a** suggest σ-coordination of the aldehyde as in [Rh(H)(pCO)(Cl)(pCHO)] (**2**) [10b]. Both the ^{1}H- and ^{13}C[^{1}H}-NMR spectra show *s*s at fields slightly modified with respect to the free ligand [15–17]. Also, the IR spectrum exhibits two absorptions due to $\tilde{\nu}$(C=O) at 1661 and 1641 cm^{-1}, at lower frequencies than those observed for the free ligand. On account of published data [14] and of the data reported below, the lower frequency can be assigned to the σ-coordinated aldehyde $\tilde{\nu}$(C=O).

An X-ray-diffraction study of **1a** was undertaken[1]). The molecular structure is shown in the *Figure*, and crystal data and selected bond distances and angles are collected in *Tables 1* and *2*. The crystal consists of [Rh(η^3-C_8H_{13})(pCO)(pCHO)]$^+$ cations and ClO_4^- anions. Provided that the η^3-C_8H_{13} ligand is taken as a bidentate ligand, the Rh-atom is coordinated in a distorted octahedral fashion. The aldehydic O-atom and the C-atom of the acyl group are in *trans*-position to each other, both atoms included in the two metallocycles, and the P-atoms and the C-atoms of the η^3-allyl moiety occupy the remaining positions. The best least-squares plane P(2)–P(1)–C(3)–C(1), with the maximum deviation of 0.08(1) Å for C(3), practically includes the Rh-atom (0.034(1) Å). This plane forms an angle of 85(1)° with the O(1)–Rh(1)–C(9) plane. The η^3-cyclooctenyl ligand adopts the expected boat-like conformation [8][18] and is bound to the Rh-atom *via* the three allylic atoms C(1), C(2), and C(3). The angle between the plane Rh(1)–P(1)–P(2) and the plane formed by the allylic C-atoms of 105(1)° is similar to the value found for a [Rh$^{\text{I}}$(η^3-C_8H_{13})] complex [8a]. Correspondingly, the distance Rh–C(2) is shorter than the distances Rh–C(1) and Rh–C(3), which are different owing to the different nature of the *trans*-positioned P-ligands. The P(1) and P(2) atoms are included in metallocycles of five and six atoms, respectively. This fact has a higher influence on the angles around the P-atoms than on the Rh–P distances (*Table 2*). The observed Rh(1)–C(9)(acyl) and C(9)=O(2)(acyl) distances fall within reported ranges [10a][19]. The short C(28)=O(1)(aldehyde) distance lies in the range reported for σ-aldehyde bonding [14–16][17b], and the Rh(1)–O(1) distance (2.30(1) Å) is longer than that observed in a very recently reported (σ-aldehyde)rhodium complex [17b] or in rhodium complexes

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[1]) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as Deposition No. CCDC-173752. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

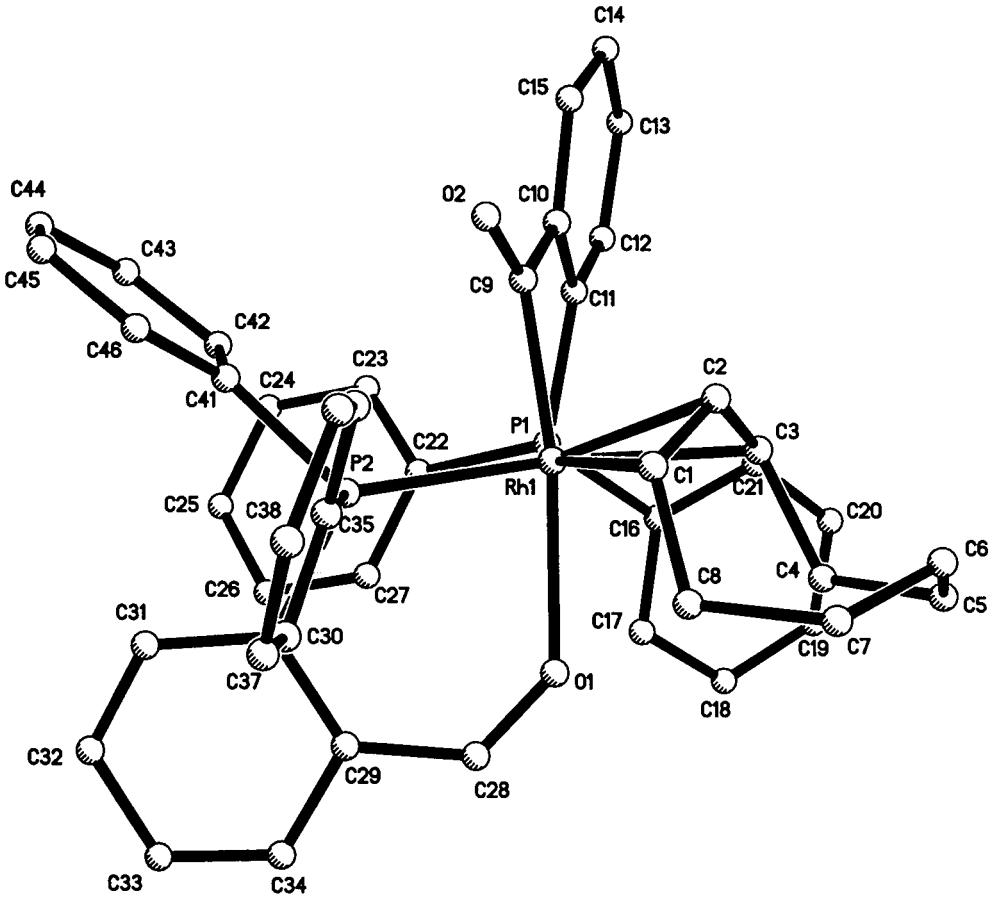


Figure. *PLUTO View of the cation of* **1a** · *0.5 $CHCl_3$ showing the atomic numbering.* The H-atoms are omitted for clarity.

containing σ-coordinated ketones [20] and can be related to the strong *trans*-influence of the acyl group [21].

Complex **1a** reacts with $[Rh(cod)(PR_3)_2]ClO_4$ (R = C_6H_5, **3**; *p*-FC_6H_4, **4**; *p*-ClC_6H_4, **5**; *p*-$MeOC_6H_4$, **6**) derivatives to give pentacoordinated (η^3-cyclooctenyl)rhodium(III) species $[Rh(\eta^3\text{-}C_8H_{13})(pCO)(PR_3)]ClO_4$ **7**–**10** (*Scheme 2*). These complexes cannot be obtained by the reaction of $[Rh(cod)(PR_3)_2]ClO_4$ with pCHO, which leads only to complete displacement of PR_3 to give **1a**. Also, **1a** remains unmodified upon addition of PR_3. Therefore, we think that the formation of complexes **7**–**10** is promoted by opening of the (phosphino-κP)aldehyde-κO chelate in **1a** followed by the oxidative addition of the aldehyde to $[Rh(cod)(PR_3)_2]ClO_4$, with transformation of the η^4-cyclooctadiene into the η^3-cyclooctenyl ligand, and exchange of the phosphine moieties. Complexes **7**–**10** may be more easily obtained by reacting $[Rh(cod)(PR_3)(acetone)]$-ClO_4 [22] prepared *in situ* with pCHO (Rh/pCHO 1:1) (*Scheme 3*). On following this

Table 1. *Crystal and Refinement Data for [Rh(η³-C₈H₁₃)(pCO)(pCHO)]ClO₄·0.5 CHCl₃* (**1a**·0.5 $CHCl_3$)

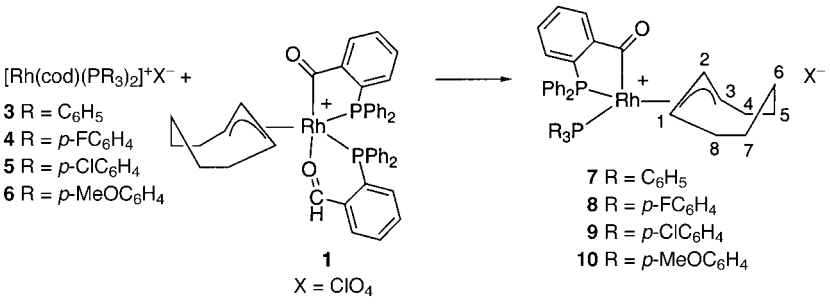
Empirical formula	$[C_{46}H_{42}ClO_6P_2Rh]1/2CHCl_3$
M_r	950.78
Crystal system	monoclinic
Space group	*P*2(1)/*n*
a/Å	10.7669(9)
b/Å	28.313(2)
c/Å	14.3658(12)
β/°	91.195(2)
Volume/Å³	4378.4(6)
Z	4
F(000)	1948
Density (calc.)/g cm^{-3}	1.442
μ/mm^{-1}	0.663
Crystal dimens./mm³	0.17 × 0.08 × 0.07
Diffractometer	*Bruker-CCD*
Radiation	graphite-monochromated MoK_α(0.71073 Å)
Scan technique	*ω* and *φ*
θ	1.44 to 25°
Data collected	$-12 \le h \le 12$, $-33 \le k \le 28$, $-17 \le l \le 17$
No. of reflns. collected	19722
No. of ind. reflns.	7399 (R(int) = 0.0832)
Structure solution	*Patterson* and *Fourier*
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	7399/3/494
$R = \Sigma[w(F_o) - (F_c)]/\Sigma(F_o)$	0.0772 (3381 obs. reflns.)
R_w[a])	0.2419
G.o.f.(F^2)	0.906
Maximum residual/e.Å^{-3}	2.20

[a]) $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

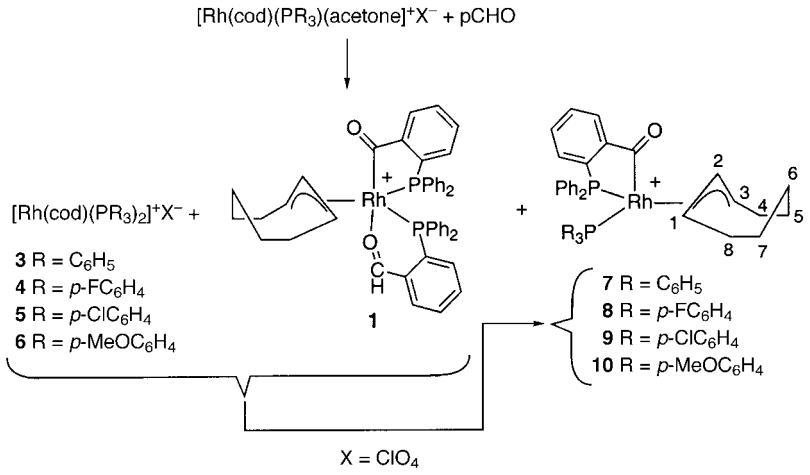
Table 2. *Selected Bond Lengths* [Å] *and Angles* [°] *for [Rh(η³-C₈H₁₃)(pCO)(pCHO)]ClO₄·0.5 CHCl₃* (**1a**·0.5 $CHCl_3$)

Rh(1)–C(1)	2.32(1)	C(1)–Rh(1)–C(2)	36.0(4)
Rh(1)–C(2)	2.16(1)	C(1)–Rh(1)–C(3)	66.2(4)
Rh(1)–C(3)	2.25(1)	C(2)–Rh(1)–C(3)	37.4(4)
Rh(1)–P(1)	2.321(3)	C(9)–Rh(1)–O(1)	170.5(3)
Rh(1)–P(2)	2.360(3)	C(9)–Rh(1)–P(1)	83.8(3)
Rh(1)–C(9)	2.01(1)	C(9)–Rh(1)–P(2)	90.1(3)
Rh(1)–O(1)	2.30(1)	C(9)–Rh(1)–C(1)	96.4(4)
P(1)–C(11)	1.80(1)	C(9)–Rh(1)–C(3)	96.2(4)
P(1)–C(16)	1.84(1)	O(1)–Rh(1)–P(1)	91.9(2)
P(1)–C(22)	1.82(2)	O(1)–Rh(1)–P(2)	83.4(2)
P(2)–C(30)	1.84(1)	O(1)–Rh(1)–C(1)	91.1(3)
P(2)–C(35)	1.83(1)	O(1)–Rh(1)–C(3)	92.1(3)
P(2)–C(41)	1.82(1)	C(1)–Rh(1)–P(1)	155.1(3)
C(1)–C(2)	1.39(1)	C(1)–Rh(1)–P(2)	95.5(3)
C(2)–C(3)	1.42(1)	C(3)–Rh(1)–P(1)	88.9(3)
C(9)–O(2)	1.21(1)	C(3)–Rh(1)–P(2)	161.2(3)
C(28)–O(1)	1.25(1)	P(1)–Rh(1)–P(2)	109.4(1)
		C(11)–P(1)–Rh(1)	99.2(4)
		C(30)–P(2)–Rh(1)	114.8(3)

Scheme 2



Scheme 3



reaction by NMR in $CDCl_3$ at 35°, we observed, upon mixing of the reactants, immediate formation of a mixture of the corresponding new complexes $[Rh(\eta^3\text{-}C_8H_{13})(pCO)(PR_3)]ClO_4$ **7**–**10**, **1a**, and $[Rh(cod)(PR_3)_2]ClO_4$ **3**–**6** occurs. Reaction of the two latter species allows complete transformation of the reactants into the corresponding **7**–**10**.

Complexes **7**–**10** behave as 1:1 electrolytes in acetone solution [11]. On account of the spectroscopic features of **7**–**10**, we believe that these compounds adopt a square-pyramidal geometry, provided that the η^3-C_8H_{13} ligand is taken as a bidentate ligand, with the acyl group in apical position in view of its high *trans*-influence. This is the geometry reported for other structurally characterized pentacoordinated dihalo(acyl)rhodium(III) compounds containing *cis*-positioned phosphine ligands [23], and $[Co(\eta^3\text{-}C_8H_{13})(P(OMe)_3]_3]$ or $[Rh(\eta^3\text{-}C_3H_5)(CO)(^iPr_2PCH_2P^iPr_2)]$ also show a square-pyramidal coordination with the allylic fragment occupying two adjacent basal coordination sites [24].

The FAB-MS of **7**–**10** exhibit a molecular-ion peak, a $[M - C_8H_{12}]^+$ peak, and a $[M - C_8H_{12} - CO]^+$ peak. Their IR spectra show the $\tilde{\nu}$(C=O) absorption of the coordinated acyl at 1675 cm^{-1}, below that corresponding to

the free ligand, and in the $^{13}C\{^1H\}$-NMR spectra, *dd*s appear at 206 ppm due to coupling with Rh ($J = 32$ Hz) and with the P-atom of pCO ($J = 7$ Hz). The $^{31}P\{^1H\}$-NMR spectra are very similar to those of **1**, with 2 *dd* corresponding to an *AMX* pattern with *cis* arrangement of the P-atoms. In the ^1H-NMR spectra, the allyl group generates a set of resonances similar to those observed for **1**, though at lower field (δ(H) 5.5 (t, $J = 8$ Hz, H–C(2)); 5.2 (m, H–C(1)); 4.2 (m, H–C(3)), and the $^{13}C\{^1H\}$-NMR spectra, showing *dd* for C(1) and C(3) at *ca.* 90 and 80 ppm, respectively, agree with a *trans*-position of these C-atoms with respect to the P-atoms. The δ(C) 21.8(s) of C(6) is characteristic for the η^3-cyclooctenyl ligand adopting a boat-like conformation [8b][13].

Pentacoordinate rhodium(III) complexes are coordinately unsaturated 16e$^-$ species. η^3-Enyl ligands bonded to saturated C-atoms may form agostic $C-H_\alpha \rightarrow M$ interactions that very frequently show fluxional behaviour, and one of the features of the agostic interaction is the ability of its displacement by donor ligands [25]. Complexes **7**–**10** do not show any resonance at $\delta(H) < 0$ ppm that would suggest an agostic interaction involving the η^3-C_8H_{13} group in the temperature range 293–193 K, and they remain unreacted when CO or H_2 is bubbled for 1 h through their solutions at atmospheric pressure and room temperature. Their reaction with pCHO was not observed, and the attempted reactions of [Rh(cod)(dppb)]ClO_4 (dppb = butane-1,4-diylbis[diphenylphosphine]) with [Rh(η^3-C_8H_{13})(pCO)(pCHO)]ClO_4 **1a** or with pCHO gave only unreacted materials. We, therefore, think that compounds **7**–**10** contain stable 16e$^-$ (η^3-cyclooctenyl)rhodium(III) species. A stable 16e$^-$ rhodacarborane (Rh^{III}) containing η^3-C_8H_{13} has been reported [25c].

Hydroformylation of olefins catalyzed by rhodium complexes has been much studied. High selectivities to the linear aldehyde have been obtained with diphosphine or diphosphite complexes [26], and P–O ligands have been found to be superior to their phosphine analogs [27]. Most of the catalyst precursors are rhodium(I) species, and rhodium(III) compounds have been scarcely studied. The hydride compound [RhH(Hdmg)$_2$(PPh_3)] (Hdmg = dimethylglyoxime monoanion) catalyses the hex-1-ene hydroformylation, while neutral [RhCl(Hdmg)$_2$(PPh_3)] or cationic [Rh(Hdmg)$_2$(PPh_3)$_2$]ClO_4 derivatives are inactive [28]. We have studied the catalytic activity of [Rh(η^3-C_8H_{13})(pCO)(pCHO)]ClO_4 **1a** in the hydroformylation of hex-1-ene at 90°. The results obtained (*Table 3*) show that, at higher pressures (80 atm), **1a** is an active catalyst, although regioselectivity to the unbranched aldehyde is observed neither without (*Entry 1*) nor with (*Entry 2*) added ligand. As can be expected [29], at

Table 3. *Hydroformylation of Hex-1-ene with the Catalyst Precursor [Rh(η^3-C_8H_{13})(pCO)(pCHO)]$^+$/3PR_3*[a])

Entry	PR_3	*p* [atm]	% Conversion (time [h])	% Heptanal	% Isoheptanal
1	–	80	99 (4)	50	50
2	pCHO	80	99 (4)	51	49
3	–	30	54 (15)	52	48
4	pCHO	30	55 (15)	68	32
5	$P(OPh)_3$	30	93 (15)	66	34
6	PPh_3	30	98 (15)	72	28
7	PPh_3[b])	30	54 (15)	68	32

[a]) Conditions: *T* 90°, CO/H_2 1 : 1, substrate/precursor 400 : 1, precursor molar concentration $6.67 \cdot 10^{-3}$ M in 1,2-dichloroethane. [b]) *T* 65°.

lower pressures (30 atm) and in the presence of added phosphine (pCHO), the regioselectivity increases, though the rate decreases markedly (*Entry 4*). The addition of $P(OPh)_3$ (*Entry 5*) or PPh_3 (*Entry 6*), instead of pCHO, to **1a** increases the rate with analogous regioselectivity. Decreasing the temperature (65°) results only in lower activity (*Entry 7*). The coordinately unsaturated Rh(III) species $[Rh(\eta^3\text{-}C_8H_{13})(pCO)(PPh_3)]ClO_4$ **7** in the presence of added PPh_3 and pCHO (**7**/PPh_3/pCHO 1:2:1) also transform hex-1-ene into heptanal, though with no regioselectivity (87% conversion after 15 h at 30 atm and 90°). These results suggest that, with **1a** as catalytic precursor, the active species may contain a P–O ligand responsible for the observed regioselectivity.

Conclusions. – Acyl(η^3-cyclooctenyl)rhodium(III) derivatives $[Rh(\eta^3\text{-}C_8H_{13})(pCO)p']$ containing two phosphine ligands *cis*-positioned to each other are formed by the oxidative addition of pCHO to cationic (cycloocta-1,5-diene)rhodium(I) complexes. Unsaturated 16e$^-$ species (p′ = triarylphosphine) are stable, and their formation requires oxidative addition of the aldehyde moiety of pCHO prior to P-coordination. When p′ = pCHO, chelate formation allows the isolation of a saturated 18e$^-$ species containing a *κO*-bonded aldehyde ligand (*σ*-coordination) as confirmed spectroscopically and by an X-ray study. The saturated 18e$^-$ species is a catalyst precursor in the catalytic hydroformylation of olefins.

Experimental Part

General. The preparation of the metal complexes was carried out at room temperature under N_2 by standard *Schlenk* techniques. $[Rh(cod)Cl]_2$ [30a], $[Rh(cod)_2]ClO_4$ [30b], $[Rh(cod)(PPh_3)_2]ClO_4$ [30c], and $[Rh(cod)(dppb)]ClO_4$ [30d] were prepared as previously reported. The 2-(diphenylphosphino)benzaldehyde (pCHO) was purchased from *Aldrich* and used as received. Conductivities were measured in acetone soln. with a *Metrohm E-518* conductimeter. IR Spectra: *Nicolet FTIR-740* spectrophotometer; KBr pellets; in cm^{-1}; range 4000 – 400 cm^{-1}. NMR Spectra: *Varian XL-300* or *BrukerAvance-500* spectrometer; $CDCl_3$ solns.; δ in ppm rel. to $SiMe_4$ as internal standard (^1H,^{13}C) and H_3PO_4 as external standard (^{31}P); *J* in Hz. MS: *VG Autospec*, liquid-secondary-ion (LSI) MS with nitrobenzyl alcohol as matrix and a caesium gun (Universidad de Zaragoza); in *m*/*z* (rel. %). Microanalyses: *Leco CHNS-932* microanalyser.

[(1,2,3-η)-Cyclooct-2-en-1-yl][2-(diphenylphosphino-κP)benzaldehyde-κO][2-(diphenyl-phosphino-κP)-benzoyl-κC]rhodium(1+) Perchlorate ($[Rh(\eta^3\text{-}C_8H_{13})(pCO)(pCHO)]ClO_4$; **1a**). To a CH_2Cl_2 soln. of $[Rh(cod)_2]ClO_4$ (0.12 mmol), a stoichiometric amount (0.24 mmol) of pCHO was added. After 30 min stirring, Et_2O was added, whereupon a yellow precipitate was formed, which was filtered off, washed with Et_2O, and vacuum-dried. Λ_M (ohm^{-1} cm^2 mol^{-1}): 120 (acetone). IR (KBr): 1661*s*, 1647*s* (C=O). ^1H-NMR ($CDCl_3$): 10.50 (*s*, CHO); 4.75 (*t*, H–C(2)); 4.41 (*m*, H–C(1)); 3.72 (*m*, H–C(3)); 1.5–0.2 (10 H, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 218.4 (*d*, *J*(Rh,C) = 28, CO); 200.9 (*s*, CHO); 113.6 (*d*, *J*(Rh,C = 4, C(2)); 90.1, 80.2 (2*dd*, *J*(Rh,C) = 6, $J(P,C)_{trans}$ = 28, C(1), C(3)); 26.2, 26.8 (*d*, *J*(P,C) = 9, CH_2(4), CH_2(8)); 26.7, 24.8 (*d*, *J*(P,C) = 4 CH_2(5), CH_2(7)); 23.4 (*s*, CH_2(6)). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 46.6 (*dd*, *J*(Rh,P) = 163, *J*(P,P) = 16, pCO); 24.0 (*dd*, *J*(Rh,P) = 155, pCHO). FAB-MS: 791 (M^+, $C_{46}H_{42}O_2{}^{103}Rh^+$; calc. 791), 683 [$M - C_8H_{12}$]$^+$, 627 ([$M - C_8H_{12} - 2CO$]$^+$). Anal. calc. for $C_{46}H_{42}ClO_6P_2Rh \cdot 0.5\ CH_2Cl_2$: C 59.82, H 4.64; found: C 59.89, H 4.64.

Reaction of Chloro[2-(diphenylphosphino-κP)benzaldehyde-κO][2-(diphenylphosphino-κP)benzoyl-κC]hydrorhodium ([Rh(H)(Cl)(pCO)(pCHO)]; **2**) *with cod and NaBPh₄*. To a CH_2Cl_2 soln. of $[Rh(cod)Cl]_2$ (0.06 mmol), a stoichiometric amount (0.24 mmol) of pCHO, was added, whereupon complete reaction to **2** and free cod was detected by ^1H and $^{31}P\{^1H\}$-NMR. Addition of a MeOH soln. of $NaBPh_4$ (0.12 mmol) followed by evaporation of CH_2Cl_2 gave $[Rh(\eta^3\text{-}C_8H_{13})(pCO)(pCHO)]BPh_4$ (**1b**), identified by NMR.

[Rh(cod)(PR₃)₂]ClO₄ (R = *p*-FC_6H_4, **4**; R = *p*-ClC_6H_4, **5**; R = *p*-$MeOC_6H_4$, **6**). To a CH_2Cl_2 soln. of $[Rh(cod)_2]ClO_4$ (0.12 mmol), a stoichiometric amount (0.24 mmol) of the corresponding phosphine, was added.

After 30 min stirring, Et_2O was added, whereupon a yellow precipitate was formed, which was filtered off, washed with Et_2O, and vacuum-dried.

[(1,2,5,6-η)-Cycloocta-1,5-diene]bis[tris(4-fluorophenyl)phosphine-κP]rhodium(+) Perchlorate (**4**): $^{31}P\{^1H\}$-NMR ($CDCl_3$): 24.2 (d, J(Rh,P) = 148). Anal. calc. for $C_{44}H_{36}ClF_6O_4P_2Rh$: C 56.04, H 3.85; found: C 55.64, H 3.53.

[(1,2,5,6-η)-Cycloocta-1,5-diene]bis[tris(4-chlorophenyl)phosphine-κP]rhodium(1+) Perchlorate (**5**): $^{31}P\{^1H\}$-NMR ($CDCl_3$): 24.8 (d, J(Rh,P) = 153). Anal. calc. for $C_{44}H_{36}Cl_7O_4P_2Rh \cdot CH_2Cl_2$: C 47.97, H 3.40; found: C 47.63, H 3.57.

[(1,2,5,6-η)-Cycloocta-1,5-diene]bis[tris(4-methoxyphenyl)phosphine-κP]rhodium(1+) Perchlorate (**6**): $^{31}P\{^1H\}$-NMR ($CDCl_3$): 23.7 (d, J(Rh,P) = 146). Anal. calc. for $C_{50}H_{54}ClO_{10}P_2Rh \cdot CH_2Cl_2$: C 55.68, H 5.13; found: C 55.36, H 4.97.

[Rh(η³-C_8H_{13})(pCO)(PR_3)]ClO_4 (R = C_6H_5, **7**; R = *p*-FC_6H_4, **8**; R = *p*-ClC_6H_4, **9**; R = *p*-$MeOC_6H_4$, **10**). To an acetone soln. of $[RhCl(cod)]_2$ (0.06 mmol) and the corresponding phosphine (0.12 mmol), the stoichiometric amount (0.12 mmol) of $AgClO_4$ was added. After 30 min, the formed AgCl was filtered. The obtained soln. was evaporated and the residue dissolved in CH_2Cl_2. After the addition of pCHO (0.18 mmol), the soln. was refluxed for 3 h. The soln. was allowed to cool at r.t. and the addition of Et_2O gave yellow precipitates that were filtered off, washed with Et_2O, and vacuum-dried.

[(1,2,3-η)-Cyclooct-2-en-1-yl][2-(diphenylphosphino-κP)benzoyl-κC](triphenylphosphine-κP)rhodium(1+) Perchlorate (**7**): Λ_M ($ohm^{-1}\,cm^2\,mol^{-1}$): 124 (acetone). IR (KBr): 1675*s* (C=O). ^{1}H-NMR ($CDCl_3$): 5.53 (t, H–C(2)); 5.28 (m, H–C(1)); 4.22 (m, H–C(3)); 1.7–0.6 (10 H, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 205.8 (dd, J(Rh,C) = 32, J(P,C) = 7, CO); 116.9 (d, J(Rh,C) = 3, C(2)); 90.6, 79.5 (2dd, J(Rh,C) = 6, $J(P,C)_{trans}$ = 24, C(1), C(3)); 28.6, 27.8 (2d, J(P,C) = 6, CH_2(4), CH_2(8)); 30.9, 27.9 (2*s*, CH_2(5), CH_2(7)); 21.8 (*s*, CH_2(6)). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 52.0 (dd, J(Rh,P) = 173, J(P,P) = 15, pCO); 22.0 (dd, J(Rh,P) = 148, PR_3). FAB-MS: 763 (M^+, $C_{45}H_{42}OP_2{}^{103}Rh^+$; calc. 763); 655 ([$M - C_8H_{12}$]$^+$), 627 ([$M - C_8H_{12} - CO$]$^+$). Anal. calc. for $C_{45}H_{42}ClO_5P_2Rh$: C 62.62, H 4.90; found: C 62.72, H 5.16.

[(1,2,3-η)-Cyclooct-2-en-1-yl][2-(diphenylphosphino-κP)benzoyl-κC][tris(4-fluorphenyl)phosphine-κP]-rhodium(1+) Perchlorate (**8**): Λ_M ($ohm^{-1}\,cm^2\,mol^{-1}$): 131 (acetone). IR (KBr): 1675*s* (C=O). ^{1}H-NMR ($CDCl_3$): 5.49 (t, H–C(2)); 5.18 (m, H–C(1)); 4.20 (m, H–C(3)); 1.8–0.7 (10 H, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 206.3 (dd, J(Rh,C) = 32, J(P,C) = 7, CO); 117.0 (*s*, C(2)); 91.8, 79.4 (2dd, J(Rh,C) = 7, $J(P,C)_{trans}$ = 23, C(1), C(3)). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 51.6 (dd, J(Rh,P) = 173, J(P,P) = 14, pCO); 20.5 (dd, J(Rh,P) = 150, PR_3). FAB-MS: 817 (M^+, $C_{45}H_{39}F_3OP_2{}^{103}Rh^+$; calc. 817), 709 ([$M - C_8H_{12}$]$^+$), 681 ([$M^+ - C_8H_{12} - CO$]$^+$). Anal. calc. for $C_{45}H_{39}ClF_3O_5P_2Rh \cdot 0.5\ CH_2Cl_2$: C 56.95, H 4.20; found: C 57.29, H 4.24.

[(1,2,3-η)-Cyclooct-2-en-1-yl][2-(diphenylphosphino-κP)benzoyl-κC][tris(4-chlorophenyl)phosphine-κP]rhodium(1+) Perchlorate (**9**): Λ_M ($ohm^{-1}\,cm^2\,mol^{-1}$): 121 (acetone). IR (KBr): 1675*s* (C=O). ^{1}H-NMR ($CDCl_3$): 5.51 (t, H–C(2)); 5.20 (m, H–C(1)); 4.23 (m, H–C(3)); 1.7–0.7 (10 H, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 206.2 (dd, J(Rh,C) = 32, J(P,C) = 7, pCO); 117.0 (d, J(Rh,C) = 3, C(2)); 92.1, 79.4 (2dd, J(Rh,C) = 6, $J(P,C)_{trans}$ = 24, C(1), C(3)). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 51.7 (dd, J(Rh,P) = 173, J(P,P) = 14, pCO); 21.1 (dd, J(Rh,P) = 150, PR_3). FAB-MS: 865 (M^+, $C_{45}H_{39}Cl_3OP_2{}^{103}Rh^+$; calc. 865), 757 ([$M - C_8H_{12}$]$^+$), 729 ([$M - C_8H_{12} - CO$]$^+$). Anal. calc. for $C_{45}H_{39}Cl_4O_5P_2Rh$: C 55.93, H 4.07; found: C 55.67, H 4.06.

[(1,2,3-η)-Cyclooct-2-en-1-yl][2-(diphenylphosphino-κP)benzoyl-κC][tris(4-methoxyphenyl)phosphine-κP]rhodium(1+) Perchlorate (**10**):. Λ_M ($ohm^{-1}\,cm^2\,mol^{-1}$): 109 (acetone). IR (KBr): 1675*s* (C=O). ^{1}H-NMR ($CDCl_3$): 5.51 (t, H–C(2)); 5.28 (m, H–C(1)); 4.18 (m, H–C(3)); 1.6–0.5 (10 H, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 206.3 (dd, J(Rh,C) = 32, J(P,C) = 7, CO); 116.8 (*s*, C(2)); 89.2, 80.0 (2dd, J(Rh,C) = 6, $J(P,C)_{trans}$ = 24, C(1), C(3)). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 51.4 (dd, J(Rh,P) = 172, J(P,P) = 16, pCO); 19.0 (dd, J(Rh,P) = 149, PR_3). FAB-MS: 853 (M^+, $C_{48}H_{48}O_4P_2{}^{103}Rh^+$; calc. 853), 745 ([$M - C_8H_{12}$]$^+$), 717 ([$M - C_8H_{12} - CO$]$^+$). Anal. calc. for $C_{48}H_{48}ClO_8P_2Rh \cdot 0.25\ CH_2Cl_2$: C 59.47, H 5.02; found: C 59.30, H 4.94.

X-Ray Structure Determination of **1a**. Crystals of **1a** were grown by layering $CHCl_3$ solns. with Et_2O. The poor quality of the crystals necessitated repetition of the data collection and refinement with different crystals. Finally, a prismatic, yellow crystal glued on a glass fiber and mounted on a *Bruker CCD* diffractometer gave data good enough to properly solve the structure. A summary of the fundamental crystal data and refinement parameters is given in *Table 1*. The data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure of 20 s covered 0.3 in ω. The first 50 frames were recollected at the end of the data collection to monitor crystal decay. No appreciable drop in the intensities of standard reflections was observed. The heavy atom was located by *Patterson* and the rest of the atoms by *Fourier* synthesis. The refinement was done by full-matrix least-squares on F^2 (SHELXTL) [31]. The O-atoms of the perchlorate group were refined isotropically due to some nonresolvable disorder from the thermal motion.

After the last cycles of refinement, some diffuse electronic density was located at the *Fourier* difference. Several models were tried to solve this disorder of the solvent, and finally one half molecule of $CHCl_3$ was assigned. In spite of this, the final ΔF shows some residual electron density (*Table 1*). The H-atoms were calculated and refined as riding on a bonded C-atom with common isotropic displacement parameters. The refinement converged to $R_1(F) = 0.0779$ ($F^2 > 2\sigma(F^2)$) for reflections observed and $wR_2(F^2) = 0.2227$ (all data).

Catalytic Reactions. The hydroformylation reactions were carried out in a *Berghof* autoclave, and the reaction mixtures were magnetically stirred and electrically heated. These experiments were not performed at constant pressure, but for the amount of substrate used, the drop of pressure was never more than 3 bar. A soln. of the substrate (20 mmol), previously stirred with alumina for 24 h, and the catalyst (0.05 mmol) in 1,2-dichloroethane (7.5 ml) was introduced into the evacuated autoclave. The gas mixture (CO/H_2 1:1) was introduced to reach the required pressure, and the mixture was heated with stirring. Conversion and regioselectivity were determined by GC analysis of the crude samples.

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