Oxidative Addition/Reductive Elimination of Aldehydes and Ketones at Rhodium

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The trigonal-bipyramidal, TBP, monohydrides $[(NP_3)RhH]$ and $[(PP_3)RhH]$ undergo electrophilic attack by $MeOSO_2CF_3$ in THF to give CH_4 and the 16-electron fragments $(NP_3)Rh^+$ and $(PP_3)Rh^+$, respectively [$NP_3 = N(CH_2CH_2PPh_2)_3$; $PP_3 = P(CH_2CH_2PPh_2)_3$]. The $(NP_3)Rh^+$ fragment inserts across sp^2 C–H bonds of aliphatic and aromatic aldehydes to yield stable Rh(III) cis hydrido acyl complexes of general formula $[(NP_3)Rh(H)(COR)]^+$ (R = H, Me, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, CH=CHCH=CO, *trans*-MeCH=CH, *trans*-PhCH=CH). These can be isolated as tetraphenylborate salts. Under the same conditions, the $(PP_3)Rh^+$ fragment is unable either to directly activate aldehydes or to keep hydride (or alkyl) and acyl groups in mutually cis positions of the coordination sphere. As a matter of fact, protonation with $HOSO_2CF_3$ or alkylation with $ROSO_2CF_3$ (R = Me, Et) of the TBP σ-acyl complexes $[(PP_3)Rh(COR)]$ (R = Me, Ph) promotes the reductive elimination of aldehydes or ketones, respectively. Reaction of the $(PP_3)Rh^+$ fragment with HCHO in THF results in the decarbonylation of formaldehyde and formation of the TBP carbonyl $[(PP_3)Rh(CO)]^+$. Both the NP_3Rh and the PP_3Rh systems react with acrolein to yield, regardless of the temperature, the η^2-alkene derivatives $[LRh\{\eta^2\text{-}CH_2{=}CH(CHO)\}]^+$ (L = NP_3, PP_3), which exhibit fluxional behavior in solution. When propargylaldehyde, HC≡CCHO, is used, cis hydrido acetylide derivatives of formula $[LRh(H)(C{\equiv}CCHO)]^+$ are obtained (L = NP_3, PP_3), thus indicating that the cleavage of the sp C–H bond prevails over that of the formyl sp^2 C–H bond. The $(NP_3)Rh^+$ and $(PP_3)Rh^+$ fragments react with *o*-(diphenylphosphino)benzaldehyde, PCHO, yielding cis hydrido acyl complexes, in which a phosphine donor of the tripodal ligands is replaced by the PCHO phosphorus atom.

Introduction

Hydridoacylmetal complexes constitute useful model compounds to gain insight into several important homogeneous catalytic processes such as the decarbonylation of aldehydes, the hydroformylation of olefins, and, in general, all of those processes that require C–H bond activation of the CHO functionality at a some stage of the catalytic cycle.[1-8]

The scarcity of stable metal acyl hydrides[9-13] is generally due to their propensity either to decarbonylate or to reductively eliminate the aldehyde. It is therefore reasonable that most of the hydrido acyls reported in the literature contain iridium, i.e. a metal which forms strong bonds with hydrogen and carbon atoms and whose compounds exhibit remarkable kinetic inertness.[14-20] In contrast, the number of stable hydrido acyl complexes of rhodium, which plays a more effective role than iridium in promoting homogeneous catalytic processes involving aldehydes, is very scarce. To the best of our knowledge, the only hydridoacylrhodium complexes so far reported are $[Rh(H)(PPh_3)_2(C_9H_6NCO)]$[21] and [*cis*-Rh(H)(COR)$(PMe_3)_3$Cl] (R = Me, Ph, OMe, 4-C_6H_4F).[19,22,23]

In the course of our studies on the activation of C–H and H–H bonds by rhodium(I)[24-26] and iridium(I)[27,28] in the presence of the tripodal polyphosphines $N(CH_2CH_2PPh_2)_3$ (NP_3) and $P(CH_2CH_2PPh_2)_3$(PP_3), we have recently found that the coordinatively and electronically unsaturated systems $(NP_3)Rh^+$ and $(PP_3)Rh^+$ are fairly efficient in the cleavage of C–H bonds from saturated and unsaturated hydrocarbons. We therefore decided to investigate the reactions of aldehydes with the $(NP_3)Rh^+$ and $(PP_3)Rh^+$ fragments.

A preliminary account of part of this work has been already published.[29]

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Table I. Analytical and Chemical-Physical Data for the Complexes

compd	anal. found[a] C	H	N	Rh	yield, %	Λ, Ω^{-1} cm^2 mol^{-1}	IR, cm^{-1} ν(RhH)	ν(CO)	other
3	72.15 (72.77)	5.91 (5.83)	1.22 (1.27)	9.09 (9.30)	80	57	2020	1640	
4	72.82 (72.93)	6.03 (5.94)	1.17 (1.25)	8.99 (9.11)	85	55	1990	1630	
5	74.01 (74.18)	5.91 (5.80)	1.09 (1.18)	8.43 (8.71)	85	53	2050	1610	
6	74.12 (74.25)	6.10 (5.98)	1.08 (1.17)	8.50 (8.60)	80	56	2050	1615	
7	73.13 (73.27)	5.99 (5.90)	1.02 (1.15)	8.21 (8.48)	75	56	2050	1605	ν(OMe) 1260
8	72.60 (72.77)	5.81 (5.68)	1.15 (1.19)	8.39 (8.78)	75	52	2060	1590	
9	73.06 (73.37)	6.15 (5.98)	1.11 (1.22)	8.67 (8.98)	80	49	2050	1600	ν(C=C) 1640
10	74.32 (74.57)	5.86 (5.84)	1.10 (1.16)	8.40 (8.52)	85	53	2010	1580	ν(C=C) 1630
11	73.15 (73.22)	5.92 (5.88)	1.22 (1.24)	9.03 (9.09)	90	55		1660	
12	73.46 (73.35)	5.80 (5.71)	1.02 (1.24)	8.94 (9.11)	60	50	2050	1630	ν(C≡C) 2100
13	74.32 (74.73)	5.70 (5.53)	0.89 (1.02)	7.37 (7.53)	60	50	1985	1630	
15	72.25 (72.26)	5.74 (5.62)		8.88 (8.97)	80	56		1660	
16	71.95 (72.14)	5.84 (5.79)		8.72 (8.96)	55	54	2000	1630	ν(C≡C) 2085
23	73.09 (73.25)	5.86 (5.66)		8.21 (8.31)	30	126	1985	1620	

[a] Calculated values are given in parentheses.

Experimental Section

General Data. All the solvents were reagent grade and were used as received. Tetrahydrofuran (THF) was purified by distillation over $LiAlH_4$ under nitrogen just prior to use. The compounds [(NP_3)RhH] (1), [(PP_3)RhH] (14), [(PP_3)RhCl] (22), [(PP_3)RhR] [R = Me (18), Ph (19)], and [(PP_3)Rh(COR)] [R = Me (20), Ph (21)] were prepared as described in ref 26. Aldehydes were purchased from commercial suppliers and purified by distillation just before the use. The ligand PP_3 was purchased from Strem Chemicals.

Propargylaldehyde[30] and *o*-(diphenylphosphino)benzaldehyde[31] (PCHO) were prepared according to the literature methods. The ligand NP_3 was synthesized as previously described.[32] Gaseous formaldehyde was generated by heating paraformaldehyde in a slow stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer using samples mulled in Nujol between KBr plates. Proton NMR spectra were recorded at 300 MHz on a Varian VXR 300 spectrometer. Peak positions are relative to Me_4Si as an internal reference. $^{31}P\{^1H\}$ NMR spectra were recorded on Varian CFT 20 and Varian VXR 300 instruments operating at 32.19 and 121.42 MHz, respectively. Chemical shifts are relative to external H_3PO_4 85% with downfield values reported as positive. Conductivities were measured with a WTW Model LBR/B conductivity bridge. The conductivity data were obtained at sample concentrations of ca. 1×10^{-3} M in nitroethane solutions.

GC analyses were performed on a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector and a 6-ft 0.1% SP-1000 on Carbopack C $^1/_8$ in. stainless-steel column (Supelco Inc.). Quantification was achieved with a Shimadzu C-R6A Chromatopac coupled with the chromatograph, operating with an automatic correct area normalization method.

The $^{31}P\{^1H\}$ NMR spectra of the PCHO complexes **13** and **23** were simulated by use of an updated version of the LAOCN3 program.[33] The initial choices of shifts and coupling constants were refined by successive iterations, the assignment of the experimental lines being performed automatically. The final parameters gave a fit to the observed line positions better than 0.6 Hz.

Synthesis of the Complexes. All reactions were routinely performed under dry oxygen-free nitrogen by using standard Schlenkware. The solid compounds were collected on sintered glass frits and washed, unless otherwise stated, with ethanol and *n*-pentane before being dried in a stream of nitrogen.

Yields, microanalytical data, conductivity values, and selected IR absorbances for all of the compounds are collected in Table I.

Preparation of [(NP_3)Rh(H)(COH)]BPh_4 (3). A suspension of **1** (0.30 g, 0.40 mmol) in THF (25 mL) was treated with a slight excess of $MeOSO_2CF_3$ (60 μL, 0.54 mmol) at 0 °C under magnetic stirring. In a few minutes the starting yellow hydride dissolved while the solution turned colorless. Gaseous formaldehyde from paraformaldehyde (0.20 g) was carried in a slow stream of nitrogen into the solution, which was stirred for an additional hour. During this time the solution turned clear yellow. On addition of solid $NaBPh_4$ (0.40 g, 1.17 mmol) and ethanol (25 mL), followed by slow evaporation of the solvent, colorless crystals of **3** were obtained, which were recrystallized from acetone/ethanol.

Preparation of [(NP_3)Rh(H)(COR)]BPh_4 [R = Me (4), Ph (5), 4-MeC_6H_4 (6), 4-$MeOC_6H_4$ (7), CH=CHCH=CO (8), *trans*-MeCH=CH (9), *trans*-PhCH=CH (10)]. A suspension of **1** (0.30 g, 0.40 mmol) in THF (25 mL) was treated with a slight excess of $MeOSO_2CF_3$ (60 μL, 0.54 mmol) at 0 °C under magnetic stirring. In a few minutes the starting yellow hydride dissolved while the solution turned colorless. A slight excess of the appropriate aldehyde was added and the solution stirred for 1 h. On addition of solid $NaBPh_4$ (0.40 g, 1.17 mmol) and ethanol (25 mL) to the resulting yellow solutions, followed by slow evaporation of the solvent, colorless crystals of **4–10** were obtained, which were recrystallized from acetone/ethanol.

Preparation of [(NP_3)Rh{η^2-CH_2=CH(CHO)}]BPh_4 (11). The above reported procedure for **9** was successfully employed for the synthesis of this red-orange compound except for substitution of acrolein for cynnamaldehyde.

Preparation of [(NP_3)Rh(H)(C≡CCHO)]BPh_4 (12). This compound was prepared as pale cream crystals by a similar procedure as for **4** except for substitution of propargylaldehyde for acetaldehyde.

Preparation of [(NP_3)Rh(PCHO)]BPh_4 (13). The method reported above for **4** was used for the preparation of this yellow compound except for substitution of *o*-(diphenylphosphino)-benzaldehyde for acetaldehyde.

Reaction of [(PP_3)RhH] with $MeOSO_2CF_3$ and Formaldehyde. To a well-stirred solution of **14** (0.40 g, 0.52 mmol) in THF (20 mL) was added neat $MeOSO_2CF_3$ (65 μL, 0.59 mmol) via syringe at 0 °C. The starting yellow color immediately disappeared to produce a deep purple solution. After 5 min gaseous formaldehyde from 0.20 g of paraformaldehyde was delivered into the solution by means of a stream of dry nitrogen. There was a slow color change from purple to red orange and, finally, to yellow. Concomitant hydrogen evolution was observed by GC. Addition of 25 mL of ethanol containing 0.50 g (1.46 mmol) of $NaBPh_4$ precipitated yellow microcrystals of [(PP_3)Rh(CO)]BPh_4 (17).

Reaction of 14 with $MeOSO_2CF_3$ and Acrolein. Freshly distilled acrolein (0.5 mL, 7.50 mmol) was added to a THF solution of $(PP_3)Rh^+$ prepared in situ by reacting **14** (0.40 g, 0.52 mmol)

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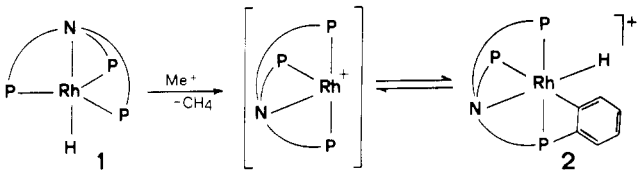
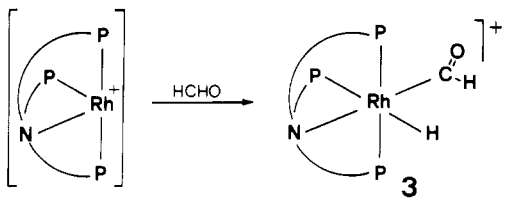
Scheme I



Scheme II



with $MeOSO_2CF_3$ (65 μL, 0.59 mmol). The solution turned immediately red-orange and separated, after addition of $NaBPh_4$ (0.40 g, 1.17 mmol) and ethanol, red crystals of $[(PP_3)Rh\{\eta^2\text{-}CH_2{=}CH(CHO)\}]BPh_4$ (**15**).

Reaction of 14 with $MeOSO_2CF_3$ and Propargylaldehyde. Addition of neat HC≡CCHO (0.30 g, 5.55 mmol) to a well-stirred THF (20 mL) solution of **14** (0.40 g, 0.52 mmol) and $MeOSO_2CF_3$ (65 μL, 0.59 mmol) produced a fast disappearance of the red-purple color typical of the $(PP_3)Rh^+$ system. Addition of $NaBPh_4$ (0.30 g, 0.88 mmol) and ethanol (15 mL) gave colorless crystals of the hydrido acetylide complex $[(PP_3)Rh(H)(C{\equiv}CCHO)]BPh_4$ (**16**).

Reaction of 14 with $MeOSO_2CF_3$ and PCHO. Reaction of PCHO (0.12 g, 0.41 mmol) with a deep red solution of **14** (0.40 g, 0.52 mmol) and $MeOSO_2CF_3$ (65 μL, 0.59 mmol) gave, after usual workup, the dinuclear complex $[\{(PP_3)Rh\}_2(PCHO)](BPh_4)_2$ (**23**).

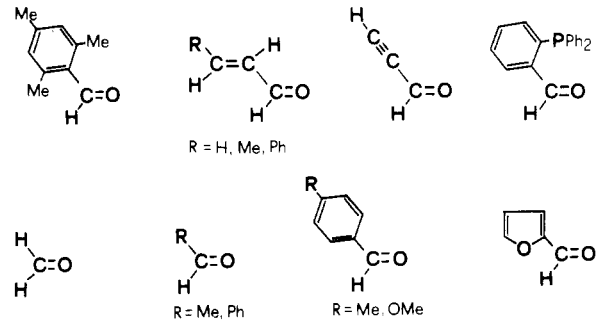
Results and Discussion

Reactivity of the $(NP_3)Rh^+$ Fragment with Aldehydes. The reaction of $[(NP_3)RhH]$ (**1**), dissolved in THF, with a slight excess of $MeOSO_2CF_3$, results in the evolution of methane and consequent formation of the 16-electron fragment $(NP_3)Rh^+$.[24,26] In the absence of added ligands, the latter readily inserts across a C–H bond from a phenyl substituent on one of the phosphine donors of the tripodal ligand to give the ortho-metalated hydride $[\{(Ph_2PCH_2CH_2)_2N(CH_2CH_2PPhC_6H_4)\}Rh(H)](OSO_2CF_3)$ (**2**) (Scheme I). It is well-known that the intramolecular cyclometalation reaction can be reversed by a plethora of organic and inorganic reagents, including monofunctional ligands, alkenes, alkynes, arenes, heteroallenes, dihydrogen, and carbon monoxide.[24,26] We have now found that aldehydes also readily shift the equilibrium toward the butterfly-shaped $(NP_3)Rh^+$ fragment via addition to **2**.

In a typical procedure, gaseous formaldehyde is delivered by a stream of nitrogen into a THF solution of the ortho-metalated hydride **2** prepared as shown in Scheme I. The colorless solution is slowly concentrated, and then $NaBPh_4$ in ethanol is added. Within a few minutes, colorless crystals of the hydrido formyl complex $[(NP_3)Rh(H)(CHO)]BPh_4$ (**3**) precipitate (Scheme II).

Compound **3**, which represents the first stable example of hydrido formyl complex of rhodium, is air-stable and can be recrystallized from acetone/ethanol mixtures even in aerobic conditions. It is soluble in common organic solvents including nitroethane in which it behaves as a 1:1 electrolyte (Table I). The presence of the BPh_4 anion is confirmed by microanalytical data as well as IR spectroscopy which shows the typical band at 610 cm^{-1} and a reinforced phenyl vibration at 1580 cm^{-1}. Also, the IR spectrum contains absorbances at 2020 (m) and 1640 (s) cm^{-1}. Both the position and the intensity of these two bands diagnose the presence of terminal hydride and σ-formyl ligands. The steric requirements of the tripodal ligand and the NMR spectroscopic characterization of the compound (vide infra) allow one to assign an octahedral geometry to **3**, in which the hydride and formyl ligands occupy mutually cis positions of the coordination polyhedron. Indeed, the $^{31}P\{^1H\}$ NMR spectrum (Table III) exhibits a well-resolved first-order AM_2X pattern consistent with C_{2v} symmetry of the $(NP_3)Rh$ fragment.[26] The resonance due to the two equivalent, mutually trans, phosphorus atoms, P_M, appears as a doublet of doublets and arises from coupling to the equatorial phosphorus atom, P_A, and to the rhodium nucleus. The lower field signal consists of a large doublet of triplets due to coupling to the two axial phosphorus atoms and to rhodium. The octahedral structure of **3** is positively supported also by the proton NMR spectrum, which exhibits, in addition to the resonances due to the methylenic and aromatic protons of the tripodal ligand, two signals, each of which corresponds to one proton. The resonance at higher frequency (δ = 13.37 ppm) appears as a complex multiplet and is assigned to the formyl proton. The other signal, in the hydridic hydrogen region (δ = −7.39 ppm), consists of two well-separated doublets of triplets. This pattern is due to coupling of the hydride ligand to the trans phosphorus atom P_A, the two equivalent P_M atoms, and rhodium. On the basis of the $J(HP)$ values, it is apparent that the hydride ligand lies in the equatorial plane of the octahedron, trans to the phosphorus atom P_A. The formation of the cis hydrido formyl complex **3** is not surprising in view of the propensity of the $(NP_3)Rh^+$ fragment to cleave under mild conditions different types of C–H bonds as well as to maintain hydride and σ-organyl groups in cis positions.[24,26] Unlike the known hydrido acyl complexes of rhodium,[19,21] **3** and its congeners (vide infra) exhibit remarkable thermal robustness, a fact that makes it possible to study in detail the chemistry of this class of intriguing compounds. Indeed, most of the hydrido acyl complexes herein described do not lose dihydrogen forming carbonyl derivatives even when refluxed in THF.

Scheme III



In order to gain insight into the factors that may affect the activation of sp^2 C–H bonds of aldehydes by the $(NP_3)Rh^+$ system, we have reacted the latter fragment with a large number of aromatic and aliphatic aldehydes in which both the electronic and steric features have been varied as systematically as possible (Scheme III). The analytical and chemical–physical data for all of the new compounds obtained are provided in Table I, while the NMR data are collected in Tables II (^1H NMR spectra) and III ($^{31}P\{^1H\}$ NMR spectra).

In most instances, the formyl C–H bonds undergo oxidative breaking at rhodium in a highly stereospecific manner regardless of the nature of the organyl residue supporting the CHO function; i.e., the hydrido ligand is invariably located trans to the terminal phosphorus atom,

Table II. Selected Proton NMR Spectral Data for the New Complexes[a]

	^{1}H NMR δ^b				
complex	RhH	$J(HP_{trans})^c$	$J(HP_{cis})^c$	$J(HRh)^c$	COR
3	−7.39 ddt	139.3	7.0	17.1	13.37 m, 1 H, CHO
4	−8.20 ddt	142.0	8.0	18.0	1.24 m, 3 H, $COCH_3$
5	−8.12 ddt	154.3	10.4	16.4	*d*
6	−8.16 ddt	155.0	10.3	17.1	*d*; 3.06 s, 3 H, CH_3
7	−8.33 ddt	154.4	10.8	17.2	*d*; 3.53 s, 3 H, OCH_3
8	−7.72 ddt	154.9	8.4	16.0	6.47 m, 1 H, 6.13 m, 1 H, CH furanic ring[e]
9	−8.05 ddt	148.8	8.2	17.0	6.13 d, 1 H, CH(CO); 5.97 dq, 1 H, $CH(CH_3)$ 1.24 q, 3 H, CH_3
10	−7.72 ddt	148.0	7.9	17.1	*d*
11					8.19 m, 1 H, CHO; 3.62 b, 1 H, CH; 2.19 b, 1 H, CH; 1.42 b, 1 H, CH
12	−7.13 ddt	150.3	5.7	16.0	8.02 m, 1 H, CHO
13	−7.28 dtd	133.1	13.6	6.2	*d*
15					8.20 m, 1 H, CHO; 4.01 b, 1 H, CH; 2.67 b, 1 H, CH[f]
16	−9.12 dpq	156.3	13.1	13.1	8.17 m, 1 H, CHO
23	−8.86 dm	119.6			*d*

[a] At room temperature in acetone-d_6 solution. [b] In ppm from external TMS. The resonances due to hydrogen atoms belonging to the tripodal ligands are not reported. Key: d, doublet; t, triplet; pq, pseudoquartet; m, multiplet; b, broad. [c] Coupling constants in Hz. [d] Masked by the aromatic protons of the ligand and of the BPh_4 anion. [e] One proton of the furanic ring is masked by the aromatic hydrogen atoms. [f] One proton of the acrolein ligand is masked by the aliphatic protons of the PP_3 ligand.

Table III. $^{31}P\{^1H\}$ NMR Data for the Complexes

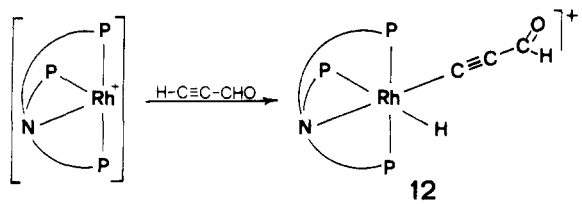
		chemical shift[a]			coupling constant *J*, Hz				
compd	pattern	$\delta(P_A)$	$\delta(P_M)$	δ (other P)	P_AP_M	P_ARh	P_MRh	other PP	other PRh
3	AM_2X	14.16	33.19		21.5	106.8	124.2		
4	AM_2X	5.93	35.32		21.6	102.9	124.1		
5	AM_2X	3.45	31.05		21.9	100.5	120.2		
6	AM_2X	3.12	30.86		21.9	100.6	120.2		
7	AM_2X	2.20	30.44		22.0	101.3	120.3		
8	AM_2X	7.95	35.63		21.2	100.1	119.6		
9	AM_2X	8.80	35.97		21.6	103.2	124.7		
10	AM_2X	9.55	36.99		21.1	103.1	124.2		
11[b]	A_3X	29.24				110.0			
12	AM_2X	23.11	37.01		19.3	92.1	100.4		
13	ABCMX[c]	36.99	−19.40	P_B, 56.88 P_C, 14.06	0.0	103.6	0.0	P_AP_B, 320.1 P_AP_C, 22.8 P_BP_C, 20.8	P_BRh, 127.7 P_CRh, 129.1
15[d,e]	AM_3X	139.23	52.44		15.9	100.3	114.7		
16[d]	AM_2QX	134.55	43.92	P_Q, 36.77	8.7	74.9	97.1	P_AP_Q, 9.3 P_MP_Q, 17.5	P_QRh, 82.9
23	$AB_3CDEFGXY$[f]								

[a] The chemical shifts (δ) are relative to 85% H_3PO_4, with positive values being downfield from the standard. The spectra were recorded in acetone-d_6 at room temperature, unless otherwise stated. [b] In $CDCl_3$ at 330 K. [c] For a labeling scheme of **13** see Figure 1. [d] P_A denotes the central phosphorus atom of the PP_3 ligand, whereas P_Q and P_M indicate the terminal PPh_2 phosphorus atoms of the same ligand. [e] In $CDCl_3$. [f] See Table IV and Figure 3.

whereas the acyl ligand lies trans to nitrogen. Steric effects do not play a signifacative role in hampering the oxidative addition of RCHO probably because the small size of the hydride ligand in the cis position mitigates the steric requirements of the $(NP_3)Rh^+$ fragment. As a matter of fact, 2-furanaldehyde or benzaldehyde are easily activated under the same conditions employed for the smaller HCHO molecule. Only when the bulkyness of the organyl group is very large as in the case of mesitylaldehyde, the reaction is inhibited at all.

It has been previously reported by us that the $(NP_3)Rh^+$ fragment readily inserts across arene sp^2 and acetylene sp C–H bonds.[24,26] When aromatic aldehydes such as PhCHO, 4-MeC_6H_4CHO, 4-$MeOC_6H_4CHO$, and CH=C-HCH=C(CHO)O are reacted with the $(NP_3)Rh^+$ fragment, the only species formed are the cis hydrido aroyl complexes with no cuncurrential activation of the aromatic C–H bonds. Analogously, when the reactions are carried out in THF/benzene mixtures (1:10), the benzene molecule, although in large excess, is not activated. Crossover experiments carried out by using equimolar mixtures of aliphatic and aromatic aldehydes prove that the activation of the formyl group takes place for both reagents but the less bulky aldehydes are preferentially activated. As an example, a 1:1 mixture of MeCHO and PhCHO yields the corresponding hydrido acyl derivatives in a 3:1 ratio.

Scheme IV



12

Quite different is the behavior of propargylaldehyde, HC≡CCHO. In this case, the cleavage of the more acidic sp C–H linkage prevails over that of the aldehydic sp^2 bond. As a result, the only product of the reaction, even at low temperature (230 K), is the hydrido σ-acetylide complex $[(NP_3)Rh(H)(C{\equiv}CCHO)]BPh_4$ (**12**) (Scheme IV). Compound **12** is a pale cream crystalline solid, quite stable in air in the solid state and in deoxygenated solutions. It is soluble in common organic solvents, including acetone and nitroethane in which it behaves as a 1:1 electrolyte. The IR spectrum exhibits three significant absorbances: a medium intensity band at 2100 cm^{-1} assigned to the stretching vibration of a rhodium σ-acetylide triple bond, a broad band at 2050 cm^{-1} attributed to ν(Rh–H), and a

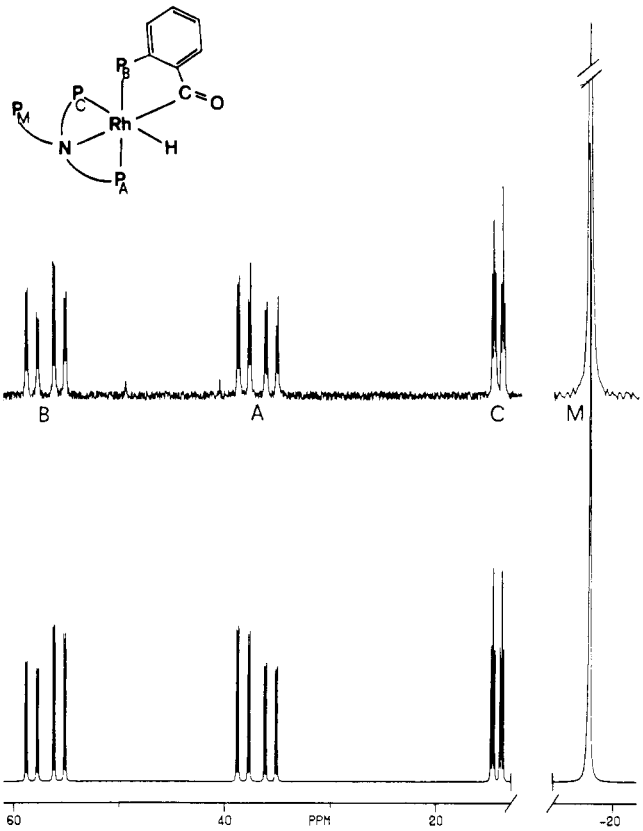


Figure 1. Experimental (upper) and computed (lower) $^{31}P\{^1H\}$ NMR spectra of **13** (acetone-d_6, 298 K, 121.42 MHz, 85% H_3PO_4 reference).

strong band at 1630 cm^{-1} which is due to the stretching mode of the carbonyl group of the uncoordinated CHO substituent. The ^1H NMR spectrum displays a high-field doublet of doublets of triplets at δ −7.13 ppm readily assignable to the hydride ligand and a low-field multiplet at δ 8.02 ppm due to the formyl proton. Finally, the $^{31}P\{^1H\}$ NMR spectrum, exhibiting a first order AM_2X splitting pattern, is fully consistent with an octahedral geometry of the complex cation.

It has been previously shown that transition-metal–ligand systems that are intrinsically reluctant to cleave C–H bonds from aldehydes, are often persuaded to do it when the formyl group is incorporated into a chelating ligand.[34] With use of this approach, Suggs was able to isolate the first examples of hydrido acyl complexes of late transition elements.[21] Generally, the "chelate assisted" oxidative addition of aldehydes is associated with the replacement of previously coordinated ligands by either the hydride or the acyl fragments. We have examined the reactivity of the $(NP_3)Rh^+$ fragment toward a typical chelating aldehyde such as *o*-(diphenylphosphino)benzaldehyde, PCHO. The reaction gives a yellow microcrystalline solid of formula $[(NP_3)Rh(PCHO)]BPh_4$ (**13**). The IR spectrum of the compound contains a strong ν(C=O) band at 1630 cm^{-1}, some 70 cm^{-1} lower than the analogous band in free PCHO. The position of this absorption is in the proper region of the chelate P–C(O) ligand.[34] Precious information on the structure of **13** is provided by the $^{31}P\{^1H\}$ NMR spectrum. Figure 1 shows the experimental and simulated $^{31}P\{^1H\}$ NMR spectra and a labeled sketch of the compound. The high-field signal in the proton NMR spectrum is shown in Figure 2.

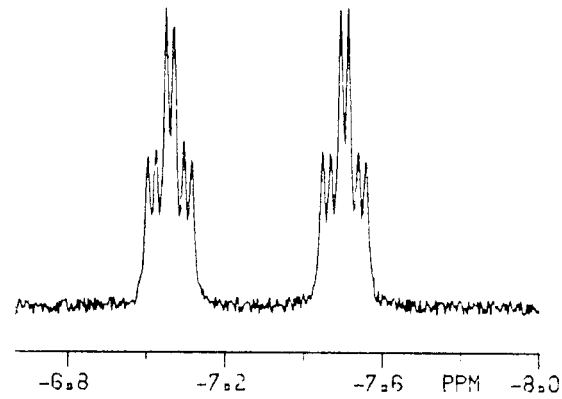


Figure 2. ^1H NMR spectrum (acetone-d_6, 298 K, 300 MHz, TMS reference) of **13**.

The room-temperature $^{31}P\{^1H\}$ NMR spectrum in acetone-d_6 exhibits a first-order ABCMX splitting pattern, consisting of four resonances of intensity ratio 1:1:1:1. The high-field signal (δ = −19.40 ppm), which is not doubled by rhodium, is safely assigned to the P_M phosphorus atom of a dangling phosphine arm of the NP_3 ligand.[35] The two lowest field resonances consist of well-resolved doublets of doublets of doublets and are assigned to the two nonequivalent phosphorus atoms P_A and P_B, which are mutually trans to each other, as put in evidence by their strong coupling [$J(P_AP_B)$ = 320.1 Hz].[36] The remaining doublet of doublets is given by coupling to rhodium [$J(P_ARh)$ = 103.6 Hz; $J(P_BRh)$ = 127.7 Hz] and to the equatorial phosphorus atom P_C [$J(P_CP_A)$ = 22.8 Hz; $J(P_CP_B)$ = 20.8 Hz]. The lowest field signal (δ = 56.88 ppm) is attributed to the phosphorus atom of the chelating phosphinoaldehyde, P_B. This assignment is supported by a comparison of chemical shifts and coordination chemical shifts of a series of related rhodium and iridium complexes of the NP_3 ligand,[24-29] as well as a family of iridium–PCHO compounds reported by Rauchfuss and Landvatter.[15] The remaining resonance at 14.06 ppm is assigned to the equatorial phosphorus atom P_C. This signal appears as a doublet of pseudotriplets as P_C is equally coupled to rhodium and to the two phosphorus atoms P_A and P_B.

The proton NMR spectrum agrees with the proposed formulation of **13**. The high-field doublet of triplets of doublets, located at −7.28 ppm, points out the presence of a hydride ligand trans to a phosphorus donor, namely, P_C [$J(HP_C)$ = 133.1 Hz]. It is interesting to remark that **13** exhibits the dtd splitting system[37] shown in Figure 1, whereas all of the other cis hydrido acyl complexes **3–10** present a ddt pattern.

Two are the possible pathways through which the reaction of the $(NP_3)Rh^+$ fragment and PCHO may proceed: (i) straightforward C–H bond oxidative addition of the PCHO formyl group to the metal, followed by replacement of a phosphine arm of the tripodal ligand by the ortho PPh_2 group; (ii) coordination of the phosphine donor of PCHO to the $(NP_3)Rh^+$ fragment with consequent formation of a TBP complex, followed by oxidative addition of the proximal formyl C–H bond to rhodium (Scheme V). In the absence of detectable intermediates, it is hard to discriminate between the two mechanisms. In fact, although apparently more complicated, mechanism (ii) has

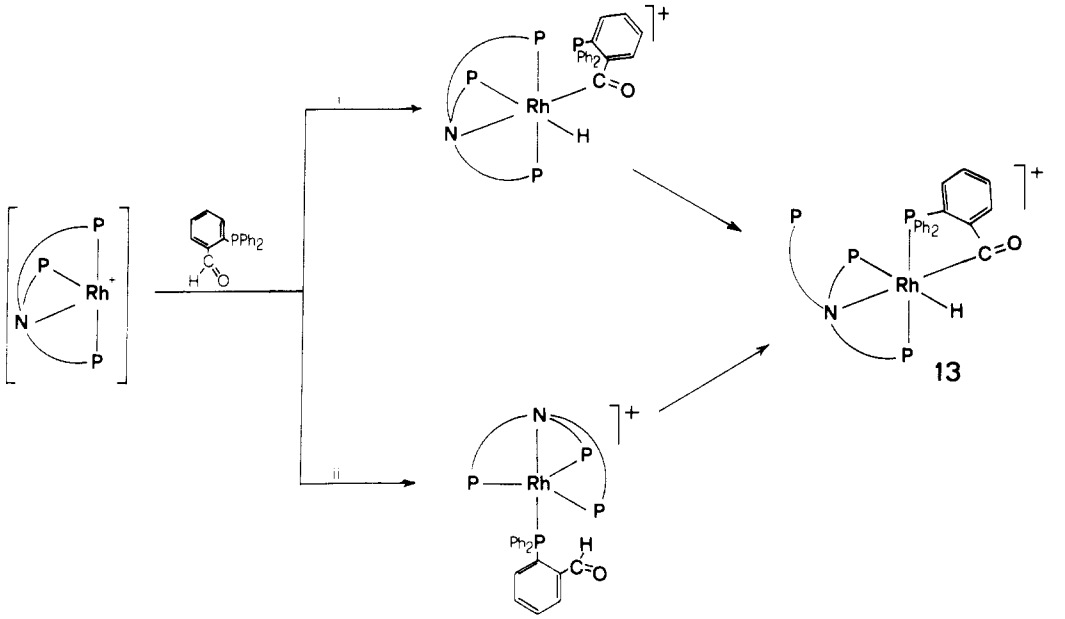
(34) Rauchfuss, T. B. In *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum: New York, 1979; Vol. 3.

(35) Bianchini, C.; Innocenti, P.; Masi, D.; Meli, A.; Sabat, *Organometallics* **1986**, *5*, 72.

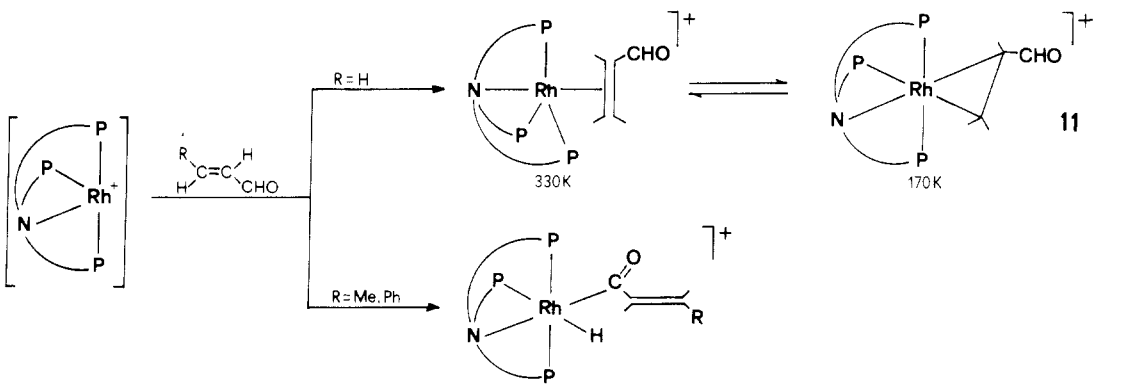
(36) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Dihel, P.; Fluck, E.; Kosfeld, R., Eds.; Springer Verlag: Berlin, 1979.

(37) Key: d, doublet; t, triplet; q, quartet; m, multiplet.

Scheme V



Scheme VI



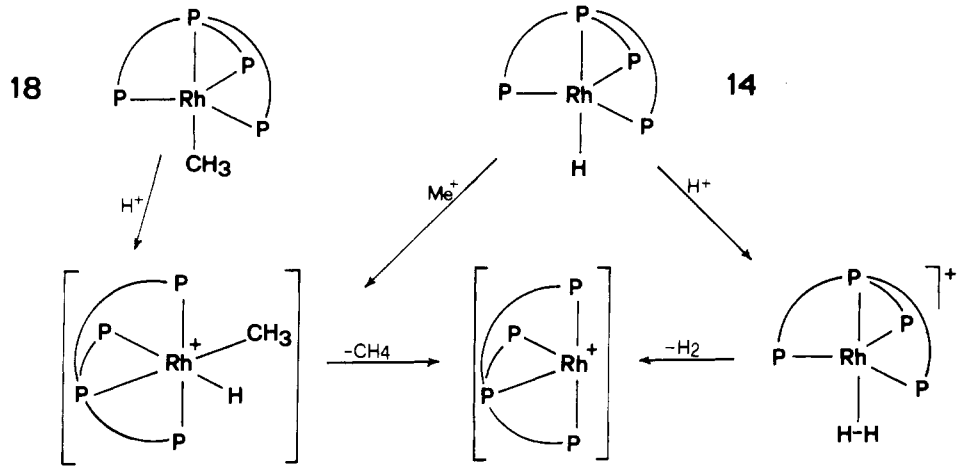
good precedents: PCHO generally acts as a simple monodentate P-donor ligand toward rhodium complexes;[34] tertiary phosphines such as PPh_3 react easily with the $(NP_3)Rh^+$ fragment yielding TBP derivatives;[38] finally, TBP Rh(I) complexes with NP_3 such as the hydride **1** and the σ-acetylide $[(NP_3)Rh(C{\equiv}CPh)]$ are able to oxidatively add C–H bonds from terminal alkynes affording octahedral Rh(III) intermediates in which the amine ligand is not coordinated to the metal.[39]

Of particular interest are the reactions of the $(NP_3)Rh^+$ fragment with unsaturated aldehydes such as $CH_2{=}CH{-}CHO$ and *trans*-$RCH{=}CHCHO$ (R = Me, Ph) in which the C—C double bond may compete with the formyl group for interaction with the metal center (Scheme VI). In effect, while cynnamaldehyde and crotonaldehyde react in the usual manner to give the cis octahedral hydrido acyl complexes **9** and **10**, respectively, acrolein coordinates the metal fragment in π fashion. The IR spectrum of the red-orange product of formula $[(NP_3)Rh\{CH_2{=}CH{-}(CHO)\}]BPh_4$ (**11**) shows no band assignable to ν(Rh—H) or ν(C=C) while the strong ν(CO) band at 1660 cm^{-1} remains essentially unshifted with respect to the free ligand. The complex cation $[(NP_3)Rh\{CH_2{=}CH(CHO)\}]^+$ is fluxional in solution as evidenced by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ at 330 K exhibits a sharp doublet centered at 29.24 ppm [J(PRh) = 110.0 Hz], which is consistent with the equivalence of the three terminal phosphorus atoms of NP_3 and an overall C_{3v} symmetry of the $(NP_3)Rh$ fragment. On lowering the temperature, the spin systems becomes more complicated and at 170 K, an AM_2X pattern appears which is typical of octahedral NP_3 complexes of rhodium with C_{2v} symmetry.[26] Additional pieces of information on the nature of the compound are provided by the proton spectrum that does not show any resonance in the hydride region, whereas a low-field multiplet of intensity 1 H, located at 8.19 ppm, may be safely assigned to the uncoordinated formyl hydrogen atom of the acrolein ligand.

The different behavior of acrolein vs cynnamaldehyde and crotonaldehyde can be easily interpreted in terms of steric crowding. In fact, we have observed that the $(NP_3)Rh^+$ moiety is able to coordinate monosubstituted alkenes such as methyl acrylate whereas it fails to link 1,2-disubstituted alkenes such as dimethyl maleate or its trans isomer dimethyl fumarate.[38] It is therefore reasonable to conclude that for 1,2-alkenes bearing a reactive substituent, and this is the case of *trans*-RHC=CH(CHO), the reactions directly occur at the -CHO functionality without involving preliminary steps such as the π-coordination of the alkene to the metal. In contrast, when only one substituent is present, the coordination of the alkene through the double bond prevails over alternative reaction

(38) Bianchini, C.; Meli, A.; Peruzzini, M., unpublished results.
(39) Bianchini, C.; Mealli, C.; Peruzzini, M.; Vizza, F.; Zanobini, F. *J. Organomet. Chem.* **1988**, *346*, C53.

Scheme VII



pathways. As a matter of fact, the π-acrolein complex **11** is quite stable and does not isomerize to the cis hydrido vinylformyl complex even after prolonged reflux in THF.

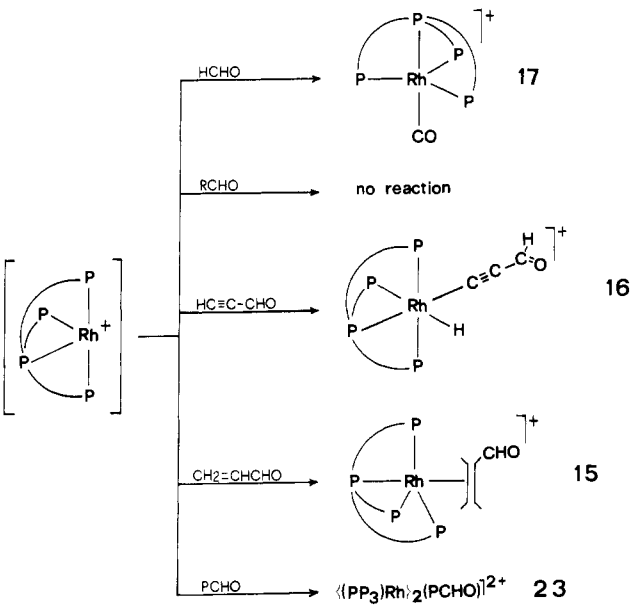
Reactivity of the $(PP_3)Rh^+$ Fragment with Aldehydes. The ability of the 16-electron fragment $(NP_3)Rh^+$ to effect the oxidative addition of aldehydes forming stable cis hydrido acyl complexes prompted us to investigate the chemistry of the isoelectronic $(PP_3)Rh^+$ fragment. The latter system can be generated by different routes[25,26] that are conveniently summarized in Scheme VII.

At variance with the NP_3 analogue, the $(PP_3)Rh^+$ moiety does not intramolecularly inserts across a C–H bond of a phenyl substituents to yield the cyclometalated congener of **2**. The elimination of methane from the unstable cis hydrido methyl complex or of dihydrogen from the η^2-H_2 complex[25] leads to the formation of the $(PP_3)Rh^+$ system, which ultimately can be stabilized by coordinating groups such as the triflate ion to give $[(PP_3)Rh(OSO_2CF_3)]$.[26] However, although not threatened by competing intramolecular reactions, the $(PP_3)Rh^+$ system does not react with aldehydes with the exception of PCHO.

The attempted reactions between the $(PP_3)Rh^+$ and various CHO-containing substrates are summarized in Scheme VIII.

The reactions with acrolein or propargylaldehyde do not differ from those of the $(NP_3)Rh^+$ system and will be briefly discussed. In contrast, quite different results have been obtained with formaldehyde and the chelating PCHO aldehyde. The reaction of the $(PP_3)Rh^+$ fragment in THF solution with an excess of freshly distilled acrolein, followed by $NaBPh_4$ addition, yields $[(PP_3)Rh\{\eta^2\text{-}CH_2{=}CH\text{-}(CHO)\}]BPh_4$ (**15**) as red air-stable crystals. The IR spectrum is quite similar to that of the corresponding NP_3 derivative and does not present any absorbance assignable to a Rh–H bond. The $^{31}P\{^1H\}$ NMR spectrum at room temperature exhibits a first-order AM_3X spin system consistent with C_{3v} symmetry of the $(PP_3)Rh$ system.[26,40] On lowering the temperature, the high-field signal, which is attributable to the three equivalent terminal P atoms of the PP_3 ligand, collapses into two broad bands of intensity ratio 1:2. Below 178 K, the spectrum becomes of the AM_2NX type. Such a temperature-dependent pattern is typical of fluxional alkene complexes of the $(PP_3)Rh$ system which have been proved to contain a η^2-bonded alkene ligand in the solid-state and low-temperature solutions.[38]

Scheme VIII



Treatment of a $[(PP_3)RhH]/MeOSO_2CF_3$·THF solution with propargylaldehyde gives, after usual workup, a white crystalline material which is air stable both in the solid state and in solution. The ^1H NMR spectrum shows resonances attributable to the presence of a hydride ligand in the high-field region and to a free formyl proton in the expected low-field part of the spectrum. The AM_2QX splitting pattern shown by the $^{31}P\{^1H\}$ NMR spectrum is consistent with an octahedral geometry of the complex. In particular, the hydride and formylacetylide ligands lie in mutually cis positions of the coordination polyhedron.[26] In nice agreement with this structure, the IR spectrum exhibits a medium $\nu(C{\equiv}C)$ band at 2085 cm^{-1}. The ^{31}P NMR spectrum without proton decoupling permits one to establish that the hydride ligand is located trans to one of the terminal PPh_2 substituents.

By reaction of $(PP_3)Rh^+$ with gaseous formaldehyde, a red-orange solution is obtained from which yellow crystals of the carbonyl $[(PP_3)Rh(CO)]BPh_4$ (**17**) can be isolated after addition of $NaBPh_4$ and ethanol. The carbonyl complex has been previously synthesized by reacting **14** with $MeOSO_2CF_3$ under CO atmosphere.[26] The present route to **17** is a typical example of formaldehyde decarbonylation by a transition-metal complex.[2,41,42] Since we

(40) Hohman, W. H.; Kountz, D. J.; Meek, D. W. *Inorg. Chem.* **1986**, *25*, 616.

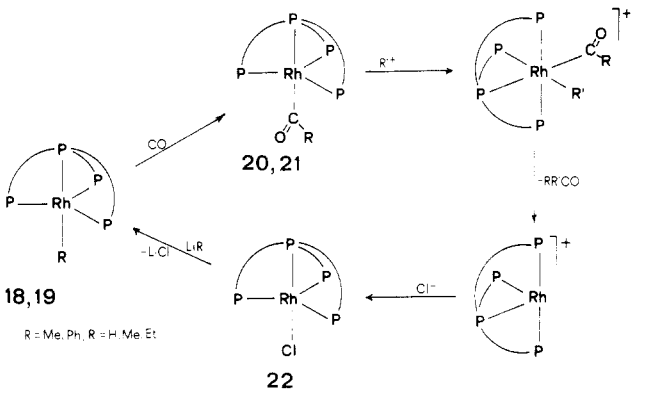
(41) Bianchini, C.; Meli, A. *Organometallics* **1985**, *4*, 1537.

Table IV. $^{31}P\{^1H\}$ NMR Chemical Shifts Values and Coupling Constants for 23[a]

			coupling constants, Hz								
	δ, ppm	pattern[b]	A	B	C	D	E	F	G	X	Y
A	142.96	ddq		21.9	277.4					89.6	
B	43.46	ddd	21.9		39.9					140.4	
C	28.16	ddqd	277.4	39.9		15.2				100.8	
D	85.65	ddpq			15.2		15.9	15.2	294.6		103.8
E[c]	36.15	ddpt				15.9		16.2	22.0		60.4
F[c]	33.84	ddpt				15.2	16.2		22.2		45.5
G	55.65	ddpt				294.6	22.0	22.2			113.5

[a] The labeling scheme is shown in Figure 3. [b] Key: d, doublet; q, quartet; pt, pseudotriplet; pq, pseudoquartet. [c] The assignments of the P_E and P_F resonances could not be done unequivocally; see text.

Scheme IX



have not been able to isolate any intermediate species during the reaction, it is extremely difficult to propose a reasonable mechanism. However, given the inability of the $(PP_3)Rh^+$ system to cleave C–H bonds from aldehydes (vide infra), the formation of a hydrido formyl intermediate appears as highly improbable. Actually, the $(PP_3)Rh^+$, generated in situ from $[(PP_3)RhH]$ and $MeOSO_2CF_3$ in THF solution, does not react with aliphatic or aromatic aldehydes even at high temperature.

In order to gain insight into the reasons for this apparently anomalous behavior, we have tried to synthesize hydrido acyl complexes of rhodium with PP_3 by an alternative route, i.e. electrophilic attack of H^+ on the TBP σ-acyl complexes of Rh^I $[(PP_3)Rh(COR)]$ [R = Me (**20**), Ph (**21**)]. These organometallics can be synthesized by the straightforward carbonylation of the corresponding σ-organyl derivatives $[(PP_3)RhR]$ [R = Me (**18**), Ph (**19**)].[26,29] Obviously, we were intrigued by the possibility of bypassing an eventual kinetic inertness of the $(PP_3)Rh^+$ fragment toward the addition of the aldehydic C–H bond. Interestingly, the addition of stoichiometric amounts of $HOSO_2CF_3$ to the canary yellow $[(PP_3)Rh(COR)]$ solutions in THF is invariably followed by the reductive elimination of the RCHO molecules (Scheme IX), thus indicating that are the thermodynamic factors to control the stability of the $[(PP_3)Rh(H)(COR)]^+$ intermediates.

In a similar way, C–C bond formation occurs at rhodium upon reaction of the σ-acyl complexes with strong alkylating agents such as $MeOSO_2CF_3$ or $EtOSO_2CF_3$. Likely, unstable cis alkyl acyl complexes form in a primary step, which undergo an irreversible reductive elimination, not prevented even at low temperature (230 K) or in the presence of a large excess of the appropriate ketone. As a matter of fact, acetone or asymmetric ketones such as EtCOMe, MeCOPh, or EtCOPh quantitatively form depending on the parent σ-acyl complex and the triflic ester used. Interestingly, the addition of THF soluble chlorides to the deep red solutions obtained after the reductive elimination step yields the TBP complex $[(PP_3)RhCl]$ (**22**) from which the starting alkyl or aryl derivative **18** or **19**, respectively, can be restored by metathetical reaction with organolithium reagents.[26]

As previously stressed, the oxidative addition of C–H bonds from aldehydes can be made easier by incorporating the formyl functionality into a polydentate chelate ligand (see the PCHO case). In fact, the presence of an anchorage point provided by the ortho PPh_2 ligand may prevent the reductive elimination of the aldehyde. Accordingly, we have reacted the $(PP_3)Rh^+$ fragment with PCHO in THF. As a result, a yellow solution is obtained from which yellow crystals of formula $[\{(PP_3)Rh\}_2(PCHO)](BPh_4)_2$ (**23**) are isolated after addition of $NaBPh_4$ in ethanol. Elemental analyses on several samples of **23** revealed that only a PCHO molecule is incorporated in the complex. The IR spectrum is very similar to that of **13**, thus indicating the occurrence of C–H bond cleavage at rhodium. In fact, the IR spectrum contains a ν(Rh—H) at 1985 cm^{-1} and ν(C=O) at 1620 cm^{-1}. The ^1H NMR spectrum exhibits a signal at δ −8.86 ppm in the hydridic hydrogen region which consists of a doublet of complex multiplets and is assigned to a hydride ligand lying trans to a phosphorus atom [$J(HP_{trans})$ = 119.6 Hz].

The structure of the new compound can be established by $^{31}P\{^1H\}$ NMR spectroscopy. The experimental and computed spectra are reported in Figure 3 together with a labeling scheme of the compound. The chemical shifts and the coupling constants are reported in Table IV.

Noticeably, unlike the NP_3 derivative **13**, all of the phosphorus atoms of **23** are bound to rhodium as put in evidence by the absence of any free signal attributable to a free PPh_2 donor group.[26,43] As we can deduce from Figure 3, compound **23** presents a seemingly complicated spin system formed by 11 magnetically active nuclei which are all nonequivalent to each other with the exception of the three phosphorus atoms P_B. The spectrum, recorded in acetone-d_6 at room temperature, exhibits a first-order pattern at 121.42 MHz and can be easily rationalized by comparing and correlating previously reported data on several rhodium complexes with NP_3 and PP_3.[26,40,43-45] Of particular utility in understanding the spectrum of **23** are the spectra of the related octahedral Rh(III) NP_3 derivative **13** and of the TBP Rh(I) complex $[(PP_3)Rh(PPh_3)]BPh_4$.[26] On this basis, the full spectrum can be formally divided into two subspectra which, however, result mutually dependent.

The first subspectrum may be related to a TBP Rh(I) complex showing an $AB_3CX(D)$ (X = Rh) pattern with a strong coupling between the P_A and P_C atoms. In turn,

(42) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1986**, *5*, 2425.

(43) Mazanek, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 85.

(44) Meek, D. W.; Mazanek, T. J. *Acc. Chem. Res.* **1981**, *14*, 266.

(45) DuBois, D. L.; Miedaner, A. *Inorg. Chem.* **1986**, *25*, 4642.

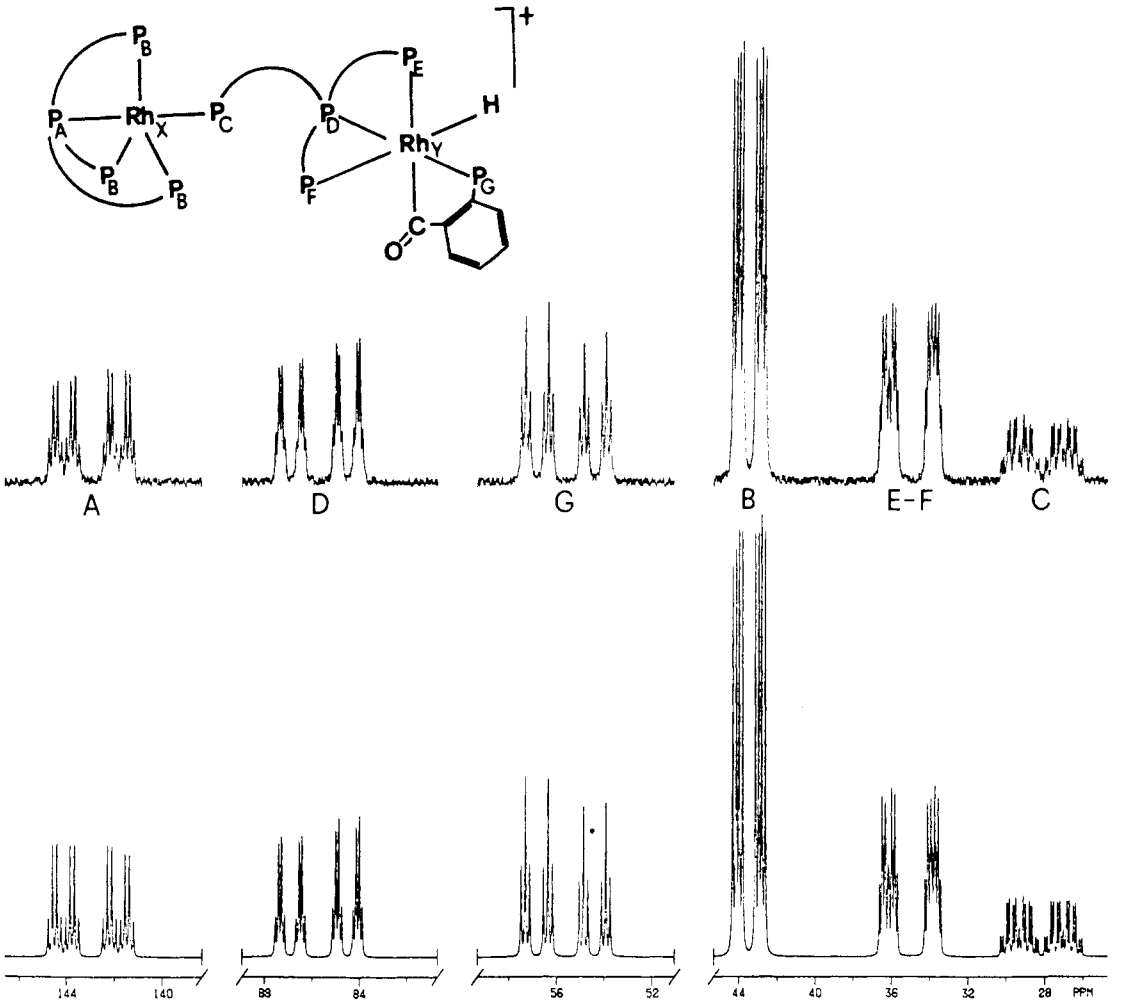


Figure 3. Experimental (upper) and computed (lower) $^{31}P\{^1H\}$ NMR spectra of **23** (acetone-d_6, 298 K, 121.42 MHz, 85% H_3PO_4 reference).

the second subspectrum may be associated with an octahedral Rh(III) system exhibiting a DEFGY(C) (Y = Rh) splitting pattern with a trans arrangement of the P_D and P_G atoms. It is worth noticing that the two subspectra exhibit only one coupling connection involving the P_C and P_D atoms [$J(P_CP_D)$ = 15.2 Hz]. Thus, they can properly be simulated as two distinct six- and five-spin systems, respectively, each of which perturbed by an external magnetically active nucleus (alternatively, P_D and P_C). The spectrum consists of seven well-separated resonances whose integral areas correspond to one phosphorus atom with the only exception of the ddd signal centered at 43.47 ppm, which is due to the three equivalent P_B phosphorus atoms. The highest and the lowest field signals complete the first subspectrum [$AB_3CX(D)$ spin system] and are assigned to the P_C and P_A atoms that are mutually trans to each other. Whereas the signal of the bridgehead phosphorus P_A exhibits the expected ddq splitting pattern, the signal of P_C is highly complicated by the additional $^3J(P_CP_D)$ coupling to the apical P_D donor of the second PP_3 molecule. As a result, a 32-line pattern is expected with partial superimposition of the central components of the multiplet. The remaining four signals form the second subspectrum [DEFGY(C) spin system]. The two resonances located at 85.61 and 55.63 ppm, each of which is split by a strong P–P coupling, are assigned to the two trans P_D and P_G atoms. The highest frequency resonance, which appears as a ddq pattern, is attributed to the central P_D atom. The quasi-coincidence of $J(P_DP_E)$,$J(P_DP_F)$, and $J(P_CP_D)$ (See Table IV) gives rise to one pseudoquartet, which is further split by Rh_Y and P_G. The other signal, consisting of a ddt pattern, is assigned to the P_G atom of the chelating PCHO molecule. This assignment is supported by the particular splitting pattern as well as the value of the chemical shift which resembles that found for the chelate PCHO ligand in the corresponding NP_3 derivative **13**. Finally, the two multiplets at 36.13 and 33.83 ppm, which are not doubled by strong coupling to a trans phosphorus atom, are attributed to the two PPh_2 phosphorus atoms of the PP_3 ligand, P_E and P_F. The small difference in the chemical shifts and the similarity between the coupling constants (Table IV) do not allow one to discriminate between the two atoms.

Registry No. **1**, 85233-91-6; **2**, 104910-92-1; **3**, 110827-41-3; **4**, 110827-43-5; **5**, 110827-45-7; **6**, 117984-84-6; **7**, 117984-86-8; **8**, 117984-88-0; **9**, 117984-90-4; **10**, 117984-92-6; **11**, 117984-94-8; **12**, 117984-96-0; **13**, 117984-98-2; **14**, 109786-30-3; **15**, 117985-00-9; **16**, 117985-02-1; **17**, 115590-97-1; **20**, 110827-46-8; **21**, 110827-47-9; **22**, 110827-50-4; **23**, 117984-82-4; PCHO, 50777-76-9; HCHO, 50-00-0; MeCHO, 75-07-0; PhCHO, 100-52-7; Md-*p*-C_6H_4CHO, 104-87-0; MeO-*p*-C_6H_4CHO, 123-11-5; (*E*)-MeCH=CHCHO, 123-73-9; (*E*)-PhCH=CHCHO, 14371-10-9; H_2C=CHCHO, 107-02-8; HC≡CCHO, 624-67-9; EtCOMe, 78-93-3; MeCOPh, 98-86-2; EtCOPh, 93-55-0; 2-formylfuran, 98-01-1; acetone, 67-64-1.