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Unusual Stereochemistry in Complexes of the Form $[RhH(CO)_2(PPr^i_3)_2]$†

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Summary: Spectroscopic studies show that $[RhH(CO)_2(PPr^i_3)_2]$ exists as three different isomers. The two major isomers are rotamers, which have trigonal-bipyramidal geometry with axial H and two equatorial phosphines (ee) distorted toward square pyramidal in such a way that the hydride can migrate rapidly through the equatorial plane between the phosphines to equilibrate the two carbonyls, while the third isomer has an axial hydride and phosphines in both axial and equatorial positions (ea).

Complexes of the form $[RhH(CO)_2(PR_3)_2]$ are key compounds in alkene hydroformylation to give aldehydes or alkene hydrocarbonylation to give alcohols. Generally, they exist as two different isomers, with the two phosphine ligands in equatorial positions (*ee*; **A** in Figure 1) or one axial and one equatorial (*ea*; **B** in Figure 1).[1] In both of these isomers, the hydride is in an axial position, either *trans* to CO (*ee*) or *trans* to P (*ea*). In most cases these two isomers interconvert at temperatures close to ambient. Many studies, mainly using bidentate ligands, have demonstrated that the relative amounts of these two isomers control the regioselectivity of hydroformylation reactions because the *ee* isomer promotes selective formation of the (usually) desired linear alkyl intermediate by hydride migration in the related $[RhH(alkene)(CO)(P)_2]$, while the *ea* isomer gives unselective H migration onto the coordinated alkene.[1] For triphenyphosphine complexes, both *ea* and *ee* isomers are also observed.[2]

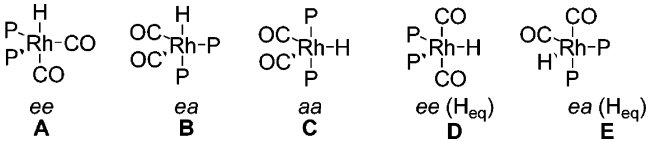

Figure 1. Possible trigonal-bipyramidal isomers for $[RhH(CO)_2(P)_2]$.

We have been studying reactions using unidentate trialkylphosphines. The interest in these systems arises because, when hydrocarbonylation reactions are carried out in protic solvents, typically alcohols, the products are alcohols rather than aldehydes.[3,4] Detailed mechanistic studies have shown that these alcohols are the primary products and that aldehydes are not intermediates. Evidence has been presented that the high electron density on the metal leads to protonation of the acyl intermediate

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Table 1. Spectroscopic Properties of $[RhH(CO)_2(PPr^i_3)_2]$ and a Related Complex

	^{31}P				^{1}H				IR
compd	$\delta(P_A)$	J_{PRh}	$\delta(P_B)$	J_{PRh}	δ(HRh)	J_{HRh}	J_{HP}	J_{HC}	ν_{CO}/cm^{-1}
$[RhH(CO)_2(PPr^i_3)_2]$ (**I**)	52.5	br	56.5	br	−9.0	7.8	99.6		2048, 1990
$[RhH(CO)_2(PPr^i_3)_2]$ (**II**)[a]	70.8	135			−10.25	4.6	4.5	4.5	2070, 2020
$[RhH(CO)_2(PPr^i_3)_2]$ (**III**)					−10.35	6.1	6.9	4.5	1965
$[RhH(CO)_2(PPr^i_3)(PPr^i_2X)]$	67.7	125	183.3[b]	132	−10.12				

[a] ^{13}C δ 204.2, br d, J_{CRh} = 61 Hz, *C*O. [b] J_{PP} = 160 Hz.

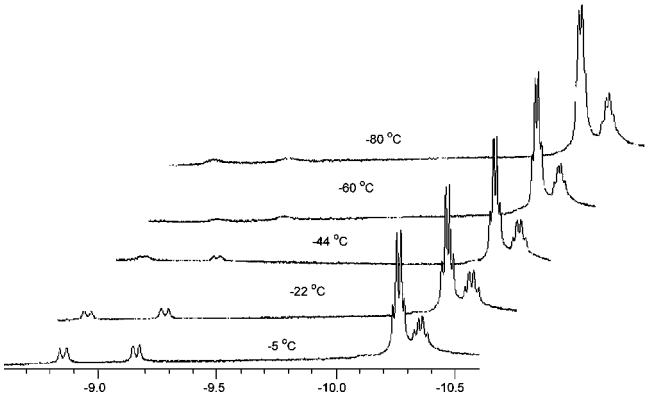


Figure 2. Hydride region of the ^{1}H NMR spectrum of $[Rh(CO)_2(acac)]$/4 PPr^i_3 under CO/H_2 (40 bar, 1:1) at different temperatures.

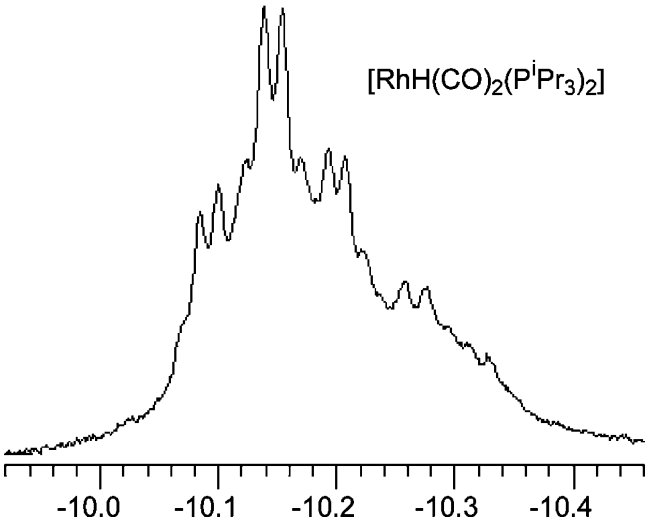
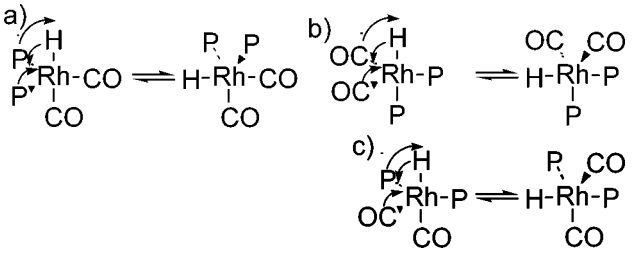


Figure 3. Part of the hydride region of the ^{1}H NMR spectrum of $[Rh(CO)_2(acac)]$/4 PPr^i_3 under $^{13}CO/H_2$ (40 bar, 1:1) at −60 °C.

to give a cationic hydroxycarbene intermediate, in which two H transfers lead directly to the alcohol product.[3,5] The regioselectivity of these reactions is relatively low ((2−3):1); therefore, studies were carried out using the bulkier trialkylphosphine PPr^i_3. Surprisingly, this gave exclusively aldehyde products (no alcohols) and the regioselectivity was also low. Model studies showed that the formation of aldehydes rather than alcohols arose because the key acyl intermediate only contains one phosphine, so that the electron density on this intermediate is too low to promote protonation.[6] In order to see whether the initial hydrido species also contains only one phosphine and to understand the reasons for the low linear selectivity, we have carried out NMR spectroscopic studies of these systems.

Scheme 1. Proposed Mechanisms for Exchange of (a) the Carbonyls in Isomer A, (b) the Phosphines in Isomer B, and (c) Isomer A with Isomer B



Solutions containing $[Rh(CO)_2(acac)]$ (acacH = 2,4-pentanedione) and 4 equiv of PPr^i_3 were examined by ^{1}H and ^{31}P NMR spectroscopy in the presence of CO/H_2 (40 bar). At room temperature, in the absence of CO/H_2, resonances are observed from the known $[Rh(\eta^1\text{-acac})(CO)(PPr^i_3)_2]$.[7] On pressurization with CO/H_2 and heating, these signals are replaced by others from a variety of complexes (Table 1).

These can be deconvoluted at low temperature, with the hydride signals (Figure 2) being most informative. Four different hydrido complexes are observed, although one (^{1}H δ −10.12; ^{31}P δ 67.7, 183.3), which is very weak, has been identified as arising from a complex derived from an impurity in PPr^i_3. The other hydrido resonances can be assigned to complexes of the type $[RhH(CO)_2(PPr^i_3)_2]$.

The resonance at δ −9.0 (J_{RhH} = 7.8 Hz, J_{PH} = 99.6 Hz, isomer **I**) can be assigned to the *ea* isomer (no exchange, **B** in Figure 1) so that coupling to the *trans* phosphine (typically ca. 100 Hz)[8,9] is observed, but the *cis* coupling is very weak. The other hydrido resonances at δ −10.25 (major isomer) and δ −10.35 appear as doublets of triplets from coupling to two equivalent P atoms and rhodium; the values of J_{HP} (<10 Hz) suggest *cis* couplings, while NMR studies under ^{13}CO show equal coupling to two CO ligands in each case (Figure 3). The ^{13}C NMR spectrum measured under ^{13}CO shows a slightly broadened doublet from the carbonyl ligands (δ 204, J_{CRh} = 61 Hz). Normally, it is expected that the *ee* isomer (**A** in Figure 1) should be the other stable isomer (apart from *ea*), but it has inequivalent carbonyls; therefore, two different carbonyl ^{13}C signals should be seen and the hydride should have two very different HC coupling constants. If there were fast exchange of the carbonyl ligands with one another, this would account for the observed NMR data, although if this exchange is fast, exchange between the *ea* and *ee* isomers would also be expected to be fast, as would exchange between the phosphines in the *ea* isomer, The exchange of the carbonyl ligands with one another cannot be dissociative, since C−P and C−hydride couplings are maintained.

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Table 2. Bond Angles and Relative Energies of $[Rh(H)(PPr^i_3)_2(CO)_2]$ in Conformations/Geometries A−C Obtained with DFT Calculations

	I (**B**)	II (lowest energy **A**)	III-1 (rotamer 1 of **II**)	III-2 (rotamer 2 of **II**)	C
Relative Energies (kcal/mol)					
bp86, SV(P) optimized	3.31	0	1.78	3.31	8.18
b3lyp, TZVP optimized	2.50	0	0.80	2.50	9.51
Bond Angles (deg) (b3lyp, TZVP Optimized Geometry)					
P1−Rh−P2	109.97	131.5	123.02	130.24	156.58
P1−Rh−C1	111.24	95.76	96.95	97.56	94.79
P1−Rh−C2	114.61	111.18	117.66	110.60	96.53
P2−Rh−C1	96.68	94.97	99.20	98.13	99.81
P2−Rh−C2	94.15	112.42	113.13	112.55	93.32
P1−Rh−H	78.00	82.00	81.00	81.00	79.00
P2−Rh−H	172.00	81.00	81.00	79.00	78.00
C1−Rh−C2	125.42	102.16	98.86	99.90	116.28
C1−Rh−H	82.00	172.00	178.00	174.00	112.00
C2−Rh−H	81.00	86.00	82.00	86.00	132.00

It has been proposed that fluxionality observed in complexes of the form $[RhH(CO)_2(P\text{-}P)]$ (P-P is a bidentate phosphine or phosphite) does not proceed by a normal Berry pseudorotation pathway but, rather, by a mechanism involving the hydride moving into the equatorial plane while two ligands in the plane move past it, as shown in Scheme 1. In this mechanism, the hydride is always axial and intermediates with equatorial hydride, which are believed to be very high in energy, are not implicated. This hydride migration type of mechanism can lead to exchange of the phosphines in the *ea* isomer (hydride passes between the two equatorial CO ligands; Scheme 1a), exchange of the COs in the *ee* isomer (hydride passes between the two equatorial P ligands; Scheme 1b), or interconversion between the *ea* and *ee* isomers (hydride passes between axial CO and P ligands; Scheme 1c).

In other cases where fluxionality has been observed in this kind of complex, P−P exchange in isomer **B** is usually more facile than exchange between the two isomers or it occurs simultaneaously.[10] For PPr^i_3 exchange between isomers **A** and **B** and exchange of the phosphines in isomer **B** are both slow at −80 °C, but if isomer **A** is indeed the major isomer observed, exchange of the carbonyls must be fast. It seems unlikely that pathway a of Scheme 1, in which the hydride passes between the two bulky phosphines, has a much lower activation energy than the other two pathways. Furthermore, for PPr^i_2Et, very similar hydride signals are observed, but the exchange of the phosphines in isomer **B** is a much lower energy pathway (only frozen out at −80 °C) than interconversion between the isomers **A** and **B** (does not occur below 100 °C). It seems counterintuitive that pathways a and b in Scheme 1 (H passing between two phosphines or two carbonyls) should have much lower activation energies than pathway c in Scheme 1 (hydride passing between CO and P). Other structures which would account for the observed equivalence of the phosphines and carbonyls would be **C** and **D** in Figure 1, both with axial H atoms. However, it has been suggested that these isomers should be of very high energy. There has been one claim[10] that such an isomer has been observed, but close analysis of the data suggests that this is an *ea* isomer (**B** in Figure 1) undergoing fast exchange of the phosphines. Finally, it is possible that the hydrides we observe have square-pyramidal geometries with axial H and either *cis* or *trans* phosphines in the basal plane. The major isomer would have to have *trans* phosphines.

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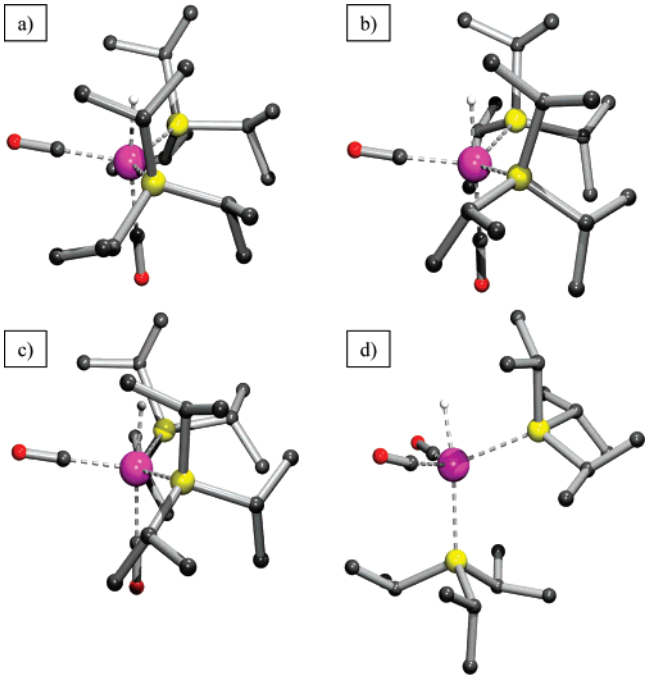

Figure 4. DFT optimized (b3-lyp, TZVP) geometries of $[Rh(H)(PPr^i_3)_2(CO)_2]$ in different conformations/geometries: (a) isomer **II** (distorted **A**); (b) possible geometry of isomer **III** (distorted **A,** rotamer 1); (c) alternative geometry of isomer **III** (distorted **A**, rotamer 2); (d) isomer **I** (**B**). Hydrogen atoms (except for the hydride) have been omitted.

Since none of the explanations offered above for the equivalence of the carbonyls and the phosphines in two of the isomers of $[RhH(CO)_2(PPr^i_3)_2]$ is completely convincing, we have carried out computational studies in order to try to model the structures.

To get an impression of the energy differences between the possible geometries **A**−**E**, we initially optimized these geometries without much consideration for the various possible conformations of the Pr^i groups of the PPr^i_3 ligands. From these studies, it became clear that the geometries **D** and **E** are not stable. Such input geometries converge to geometry **A** or **B**. Geometry **C** could be optimized as a local minimum but has a substantially higher energy than geometries **A** and **B** (Table 2). The orientations of the Pr^i groups in the PPr^i_3 ligand have little influence on the relative energy of geometry **C**, as the two PPr^i_3 ligands in mutually *trans* positions do not influence each other much. The situation is different for the geometries **A** and **B**. It turns out that for these geometries the species has many conformational local minima with varying energies, as a result of the various possible orientations of the Pr^i fragments with respect to each other. Therefore, we decided first to analyze these conformations at the semiempirical PM3 level with an automatic procedure implemented in the Spartan program package (two separate analytical runs were applied starting with different initial geometries; geometry **C** was not found among the list of >100 local minima with these semiempirical calculations). The lowest energy structures of geometries **A** and **B** arising from this analysis were then further optimized in Turbomole with DFT. Two higher lying conformations of **A** were also optimized to get a feeling for the effect of Pr^i conformations on the relative energies. Clearly, geometry **A** is the lowest energy structure. Geometry **B** lies about 2.5 kcal mol^{-1} higher in energy (Table 2).

A more detailed examination of the lowest energy structure

(Figure 4a), which broadly corresponds to the *ee* isomer (**A** in Figure 1), shows that it is significantly distorted toward square pyramidal with an axial carbonyl (C(2)O(2)) ligand and the hydride trans to C(1)O(1) in the basal plane. The best evidence for this is that the P(1)−Rh(1)−P(2) angle is increased from the 120° expected for the trigonal bipyramid to 131.49°, while the H−Rh(1)−C(1) angle is 172°, rather smaller than expected for the true trigonal bipyramid (Table 2). Such a geometry has equivalent phosphines but not equivalent carbonyl ligands. However, we propose that the opening up of the P(1)−Rh−P(2) angle allows for facile movement of the H ligand (which can be seen as through the equatorial plane of the trigonal bipyramid as in Scheme 1a or into the position *trans* to the apical CO ligand in the square pyramid). The much smaller P(1 or 2)−Rh−C(2) angles (111.18 and 112.42°) presumably prevent the hydride from passing between P and C(2) and hence make the interconversion of the *ee* and *ea* isomers a high-energy process. We assign the lowest energy structure to isomer **II**.

The structure of the *ea* isomer, **B**, is also slightly distorted (Figure 4c), with all the ligands in the equatorial plane being pushed up toward the hydride and away from the axial phosphine, but the angles between the equatorial ligands are all quite close to 120° (P(1)−Rh(1)−C(1) = 111.24°, P(1)−Rh(1)−C(2) = 114.61°, and C(1)−Rh(1)−C(2) = 125.42°), so that the hydride cannot easily pass through the equatorial plane and P−P exchange in the *ea* isomer is also a high-energy process.

This analysis explains the two most intense hydride signals observed for $[RhH(CO)_2(PPr^i)_3]$, and we tentatively assign the third (from isomer **III**, δ −10.35) to another isomer with the same basic structure as that of isomer **II** (**A**), but with a different orientation of the Pr^i groups. Two possible geometries of **III** are shown in parts b and c of Figure 4, being low-energy rotamers of **II** as obtained with the DFT calculations.

On the basis of all the data available, we conclude that, for the very bulky PPr^i_3, the key hydrocarbonylation intermediate, $[RhH(CO)_2(PPr^i_3)_2]$, exists as three different isomers, one of which has *ea* phosphines (**B** in Figure **1**), while the other two have structures similar to **A** in Figure 1 but are distorted toward a square-pyramidal geometry in such a way that carbonyl site exchange is rapid even at −80 °C. These two isomers differ from one another in having different orientations of the bulky Pr^i groups.

It is probable that the distortions from idealized geometry account for the rather low regioselectivities observed in hydroformylation reactions using Rh/PPr^i_3,[3] but this may also be exacerbated by the tendency toward the formation of monophosphine complexes.[6]

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Note Added after ASAP Publication. In the version of this paper published on the Web on June 8, 2007, the author name Paraskevi Cheliatsidou was misspelled. In addition, ^{31}P and ^{1}H NMR data for the compound $[RhH(CO)_2(PPr^i_3)(PPr^i_2X)]$ in Table 1 were either incomplete or missing. The version of the paper that now appears is correct.

Supporting Information Available: Text giving experimental details and details of the DFT calculations. This information is available free of charge via the Internet at http://pubs.acs.org.

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