stirred for 15 min, the solution was evaporated to dryness. The residue was extracted with three portions of dichloromethane; the solution was filtered and concentrated to a small volume. The crude product obtained by addition of diethyl ether, was crystallized from the same solvents to give the analytical sample (888 mg): yield 83%; dec pt >235 °C. Anal. Calcd for $C_{68}H_{58}B_2F_8Fe_2O_2P_4Pt_2$: C, 47.83; H, 3.63. Found: C, 48.08; H, 3.69. IR (Nujol; $cm^{-1}$): 3640 br, 3520 br, 3400 br, 1600 w, br.

**$[Pt_2(L-L)_2H_3][BF_4]$ (7). (a) From Compound 4.** To a stirred solution of compound **4** (549 mg, 0.492 mmol) in methanol (40 mL) was added finely ground $KBH_4$ (30 mg, 0.55 mmol) dissolved in 30 mL of the same solvent; a yellow precipitate was filtered and crystallized from dichloromethane (50 mL) and diethyl ether (50 mL) to give the yellow analytical sample by concentration (310 mg): yield 79%; mp 230 °C (dec >200 °C). Anal. Calcd for $C_{68}H_{59}BF_4Fe_2P_4Pt_2{\cdot}0.5CH_2Cl_2$: C, 50.45; H, 3.68. Found: C, 50.52; H, 3.91. IR (Nujol; $cm^{-1}$): 2035 w ($\nu_{PtH}$).

**(b) From Compound 6.** Complex **7** was obtained similarly from the binuclear species **6**, by using a $Pt/BH_4$ molar ratio of 2/1; yield ca. 50%.

**$[(L-L)Pt(\mu-H)(\mu-CO)Pt(L-L)][BF_4]$ (8).** Complex **7** (406 mg, 0.856 mmol) was suspended in acetone (40 mL) and CO was bubbled into the suspension at room temperature for 30 min. The resulting red solution was evaporated to a small volume (ca. 10 mL) and eluted through a 20 × 1 cm column of deactivated $Al_2O_3$ (10% $H_2O$). The analytical sample (215 mg; yield 52%) was obtained by addition of diethyl ether to the concentrated solution: orange; mp 230–232 °C (dec >160 °C). Anal. Calcd for $C_{69}H_{57}BF_4Fe_2OP_4Pt_2$: C, 51.33; H, 3.53. Found: C, 51.54; H, 3.68. IR (Nujol; $cm^{-1}$): 1770 s ($\nu_{CO}$).

**X-ray Data Collection and Structure Determination.** Crystal data and other experimental details are summarized in Table II. The diffraction experiment was carried out on a red prismatic crystal with an Enraf-Nonius CAD-4 diffractometer at room temperature, using monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The calculations were performed on a PDP 11/34 computer using the SDP-plus structure determination package.[28] The diffracted intensities were corrected for Lorentz effects, polarization, and absorption (empirical correction).[29] Scattering factors and anomalous dispersion corrections for atomic scattering factors of non-hydrogen atoms were taken from ref 30. No extinction correction was performed.

The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares, minimizing the function $\sum w(F_o - k|F_c|)^2$. Anisotropic thermal factors were refined for Pt, Fe, P, O, F, and C atoms. A difference Fourier computed before the last cycles of the refinement revealed the positions of all the hydrogen atoms. A refinement of the bridging hydride was attempted and resulted in reasonable Pt-H distances and thermal parameter for the hydrogen atom. All the phosphinic hydrogens were introduced in the model at calculated positions (C–H = 0.95 Å).

The atomic coordinates of the structure model are listed in Table IV.

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**Registry No.** **1**, 104413-90-3; **2**, 118299-22-2; **3**, 118299-23-3; **4**, 118299-25-5; **5**, 118299-27-7; **6**, 111338-71-7; **7**, 118299-29-9; **8**, 118299-31-3; **8a**, 118299-32-4; L-L, 12150-46-8; $Pt(COD)Cl_2$, 12080-32-9; pzH, 288-13-1; 3,5-$Me_2$pzH, 67-51-6; $K_2[PtCl_4]$, 10025-99-7.

**Supplementary Material Available:** Tables of thermal parameters, calculated positions for hydrogen atoms, all bond distances and angles, and crystallographic details (29 pages); a listing of computed and observed structure factor moduli (44 pages). Ordering information is given on any current masthead page.

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Contribution from the Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule,
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# Infrared Spectroscopic Studies on Metal Carbonyl Compounds. 24.[1] Observation of the Infrared Spectrum of an Acylrhodium Tetracarbonyl during the Hydroformylation of Olefins with Rhodium-Containing Catalyst Precursors

Marc Garland and György Bor*

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An acylrhodium tetracarbonyl, $RC(O)Rh(CO)_4$, was observed and unambiguously identified by in situ infrared spectroscopy as an intermediate in the rhodium-catalyzed hydroformylation reaction at 25 °C. Its characteristic metal carbonyl $\nu$(C–O) stretching frequencies occur at 2111 (27), 2065 (41), 2039 (65), and 2020 (100) $cm^{-1}$ (with relative intensities in parentheses); the $\nu$(C–O) of the acyl group could be observed at 1698 ± 3 $cm^{-1}$ with R = $-(C_2H_4)C(CH_3)_3$, obtained from 3,3-dimethyl-1-butene as the starting olefin. The formation of this $RC(O)Rh(CO)_4$ species was observed both with $Rh_4(CO)_{12}$ and with $CoRh(CO)_7$ as catalyst precursors. The identified $RC(O)Rh(CO)_4$ is only stable at room temperature under at least 20 bar of carbon monoxide pressure.

## Introduction

Alkyl- and acylcobalt tetracarbonyls were first prepared by Hieber and co-workers,[2] who also reported the easy uptake of carbon monoxide by alkylcobalt derivatives to form the corresponding acylcobalt compounds, as shown by eq 1. (The opposite

$$RCo(CO)_4 + CO \rightarrow RC(O)Co(CO)_4 \qquad (1)$$

reaction, i.e. the loss of the CO group of the acyl fragment, was observed only with fluoroorganic derivatives.) Subsequently, this step, playing an important role in the suggested mechanistic schemes of the catalytic cycles, was called "CO insertion", even if in some cases, e.g. for $CH_3Mn(CO)_5$, it has been shown[3] that the mechanism of the reaction is rather a methyl migration. In the case of other classes of metal carbonyls, however, as e.g. *cis*-$MX(CH_3)(CO)_2(PMe_3)_2$ (M = Fe, Ru; X = I, $CH_3$, etc.), it was demonstrated that the formation of an acetyl group from a methyl ligand proceeds effectively by cis insertion rather than by cis migration of the $CH_3$ group.[4]

The occurrence of these types of compounds in cobalt-catalyzed olefin hydroformylation[5] was first suggested by Sternberg and Wender and by Heck and Breslow.[6]

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These suggestions led one of us in 1963 to the first thorough infrared spectroscopic study of several $RCo(CO)_4$ and $RC(O)Co(CO)_4$ compounds and to the first unequivocal identification of these species in samples of the hydroformylation reaction.[7] Later in situ infrared spectroscopic studies under pressure by Whyman[8] confirmed those early spectroscopic observations.

Although various rhodium carbonyls play an important role as catalyst precursors in the olefin hydrocarbonylation reaction and the significance of their application is increasing and although $RRh(CO)_4$ and $RC(O)Rh(CO)_4$ are frequently suggested to occur in the catalytic cycles,[9] no report seems to exist on the infrared spectra of acylrhodium tetracarbonyls. Also, in the first infrared spectroscopic study on the mechanism of rhodium carbonyl catalysis, carried out by sampling rather than by in situ methods,[10] only $[Rh(CO)_2(\mu\text{-}O_2CR)]_2$ could be found, besides $Rh_4(CO)_{12}$, in the samples collected during the course of the reaction. This observation has been interpreted as an indirect indication of the presence of acylrhodium carbonyls that yield, via oxidation, the binuclear carboxylato-bridged species. The first in situ infrared spectroscopic study on rhodium carbonyl catalysis, with various precursors, has been reported by King et al.[11] These authors ascribed the new carbonyl bands observed by them to an alkylrhodium tetracarbonyl, rather than to an acylrhodium species.

Here we report that the low-temperature hydroformylation reaction can be carried out in a way that allows the practically quantitative transformation of $Rh_4(CO)_{12}$ to a hitherto unknown rhodium carbonyl species. The analysis of the in situ infrared spectra of these reaction mixtures resulted in the unequivocal identification of the new species as an acylrhodium tetracarbonyl.

## Results

During the low-temperature and low-pressure catalytic hydroformylation of 3,3-dimethyl-1-butene, starting with $CoRh(CO)_7$[12] as the catalyst precursor in *n*-hexane, new infrared absorption bands were observed in the in situ solution spectra that could not be attributed to any previously known compounds.[13] Specifically, under 2–50 bar of carbon monoxide and 2–100 bar of hydrogen, the in situ solution spectra[14] clearly showed, in addition to the familiar bands of the corresponding acyl*cobalt* tetracarbonyl, new infrared absorptions at 2111, 2065, 2039, and 1698 ± 3 $cm^{-1}$. The intensities of these absorptions decreased with time or remained constant during the course of the catalytic reaction, depending on the partial pressures of the two gases.

Since the new unknown species appeared to be stabilized by partial pressures of carbon monoxide greater than 20 bar, the further identification of this species, starting from $Rh_4(CO)_{12}$ alone as catalyst precursor, was attempted. This was done in order to eliminate the overlap with the infrared absorption bands of $RC(O)Co(CO)_4$, formed when $CoRh(CO)_7$ was used as a catalyst precursor. Previously,[15] it had been shown that the hydroformylation of 3,3-dimethyl-1-butene at low temperatures and low pressures was possible by starting from $Rh_4(CO)_{12}$ alone; however, the rate of hydroformylation was extremely slow. Additionally, a very weak infrared absorption at 2111 $cm^{-1}$ had been observed in these in situ spectra, indicating the formation of the same new carbonyl species; the rate of hydroformylation increased with longer reaction times. Therefore, given a sufficiently high partial pressure of carbon monoxide and a long enough reaction time, the positive identification of the new species seemed possible.

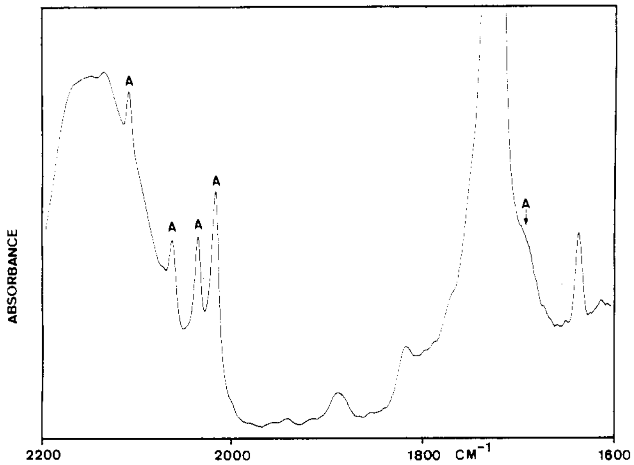

**Figure 1.** In situ infrared spectrum of the hydroformylation product, obtained from 3,3-dimethyl-1-butene (0.4 M) with the catalyst precursor $Rh_4(CO)_{12}$ (0.5 mM) at 25 °C, in 9 h reaction time (22 bar of carbon monoxide and 8 bar of hydrogen; solvent, *n*-hexane). A: absorption bands assigned to $RC(O)Rh(CO)_4$ at 2111, 2065, 2039, 2020, and 1698 ± 3 $cm^{-1}$. Cell thickness: 0.5-mm spacer.

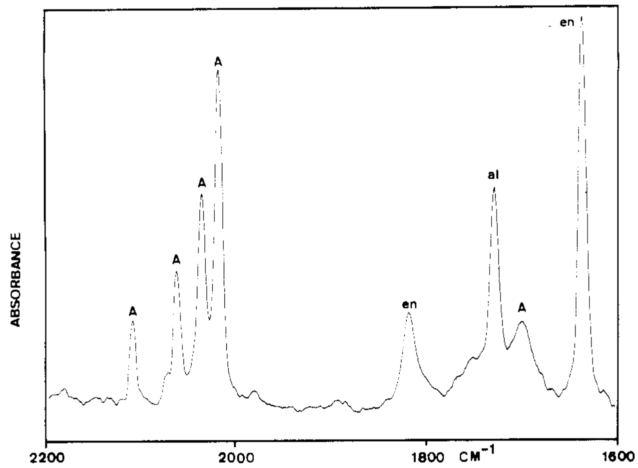

**Figure 2.** Infrared spectrum obtained from an in situ scan, after subtraction of the absorptions of the solvent, $Rh_4(CO)_{12}$, and dissolved carbon monoxide. Reaction conditions: 3,3-dimethyl-1-butene (en); catalyst precursor, $Rh_4(CO)_{12}$; CO pressure, 50 bar; $H_2$ pressure, 1 bar; temperature, 25 °C; reaction time, 48 h. The bands of $RC(O)Rh(CO)_4$ are labeled with "A"; that of the product aldehyde is labeled with "al".

In fact, the hydroformylation of 3,3-dimethyl-1-butene was successfully carried out by starting with $Rh_4(CO)_{12}$ in *n*-hexane at 25 °C.[14,16] Expecially when 50 bar of carbon monoxide and 1 bar of hydrogen were added to the solution containing the olefin and $Rh_4(CO)_{12}$, after 48 h of reaction at 25 °C, only very little hydroformylation occurred. However, about 50% of the $Rh_4(CO)_{12}$ had been transformed to the new species, and in addition to four metal carbonyl bands at 2111, 2065, 2039, and 2020 $cm^{-1}$, an infrared absorption at 1698 ± 3 $cm^{-1}$ could clearly be resolved from the relatively weak absorption of 4,4-dimethylpentanal at 1733 $cm^{-1}$. The absorption at 2020 $cm^{-1}$ could not be observed in the mixed cobalt–rhodium catalyzed system because of its overlap with a band of the acylcobalt tetracarbonyl (cf. Table I).

## Discussion

Our results are based on the in situ infrared spectra. Spectral features owing to the solvent, to dissolved carbon monoxide, and to small amounts of untransformed $Rh_4(CO)_{12}$ could be subtracted by data-processing techniques, and thus the absorption of the new

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species could be studied. Two of the typical spectra are shown in Figures 1 and 2. The first of these, Figure 1, is a "complete" spectrum of the solution in the relevant region between 2200 and 1600 cm$^{-1}$ when the hydroformylation reaction of 3,3-dimethyl-1-butene has been carried out with $Rh_4(CO)_{12}$ as the catalyst precursor at 25 °C, under 22 bar of carbon monoxide and 8 bar of hydrogen for 9 h. Even in this uncompensated spectrum, where more than 98% of $Rh_4(CO)_{12}$ has been converted to the species under study as shown by the absence of a bridging band at 1886 cm$^{-1}$ characteristic of $Rh_4(CO)_{12}$, there are four rather than three metal carbonyl C–O stretching bands at the low-energy wing of the broad band of dissolved carbon monoxide.

The spectrum in Figure 2 is of the solution obtained under 50 bar of carbon monoxide and 1 bar of hydrogen. The original spectrum has been modified by subtraction of the solvent and carbon monoxide bands and then corrected for the small amounts of $Rh_4(CO)_{12}$ present. The remaining bands after these procedures were those belonging to the olefin (at 1823 and 1641 cm$^{-1}$) and to the aldehyde formed (1733 cm$^{-1}$), together with those of a rhodium carbonyl species that will be identified.

First, it must be emphasized that the ratios of the relative intensities of the bands observed at different stages of conversion in several experiments were always the same, indicating that there is only *one* unknown species present in these samples.

The presence of four terminal $\nu$(C–O) stretching bands proves that the compound has at least four ligands. Moreover, the considerable intensity of the band at 2111 cm$^{-1}$, which belongs to the totally symmetric in-phase stretching mode,[17] proves that this is a mononuclear compound of quite low symmetry. Hence, there are only two candidates to be assigned to this spectrum: it is either an alkyl- or an acylrhodium tetracarbonyl. (A hydridorhodium carbonyl can be excluded since (i) the new species was formed only when olefin was added and (ii) we know from the observations of Vidal et al.[18] that the formation of $HRh(CO)_4$ ($\nu$(C–O) values at 2070 (m), 2039 (vs), and 2008 (w) cm$^{-1}$) requires much more drastic conditions.)

The corresponding alkyl*cobalt* tetracarbonyls, however, show only three terminal $\nu$(C–O) stretching bands.[7] This observation is in accordance with the selection rules of point group $C_{3v}$.[19] The alkylcobalt tetracarbonyls, $RCo(CO)_4$ are, according to this model, five-coordinate compounds of trigonal-bipyramidal (TBP) geometry, with the R group occupying an axial position. The sp$^3$-carbon atom at this coordination site has itself a 3-fold local symmetry, thus not influencing the main 3-fold axis of the molecule.

The acylcobalt tetracarbonyls contain a planar –C(O)R group with an sp$^2$-hybridized carbon atom. As shown by the spectrum of all $RC(O)Co(CO)_4$ compounds studied, this causes a breakdown of the $C_{3v}$ symmetry of the $Co(CO)_4$ unit irrespective of the axial or radial position of the RC(O)– group. The radial position would be the result of an alkyl-migration mechanism in the formation of the acyl compound. However, we believe, on the basis of earlier analyses of the spectra of numerous $XM(CO)_4$ derivatives (M = Co, Fe) of TBP geometry,[20] that the X heteroligands occupy prevalently the axial position. Even if the mechanism were primarily alkyl migration, a facile Berry rotation would transform the product of this step into an axial-acyl derivative. However, a distorted geometry cannot be excluded either. The highest possible symmetry of these molecules is in any case that of point group $C_s$. Therefore, we think that a "CO insertion vs alkyl migration" discussion has no relevance in the case of the compounds under study.

Since we do not see any reason to exclude the similarity of the geometry between the analogous cobalt and rhodium compounds, the early results obtained with alkyl- and acylcobalt tetracarbonyls suggest that the rhodium compound present in the catalytic solutions studied is an acylrhodium tetracarbonyl, $RC(O)Rh(CO)_4$.

**Table I.** Comparison of the $\nu$(C–O) Frequencies and Relative Intensities of the Carbonyl Bands of $C_2H_5C(O)Co(CO)_4$ and $RC(O)Rh(CO)_4$ ($R = -(C_2H_4)C(CH_3)_3$)[a,b]

| compd | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ |
|---|---|---|---|---|
| $C_2H_5C(O)Co(CO)_4$ | 2105 (27) | 2046 (54) | 2024 (81) | 2005 (100) |
| $RC(O)Rh(CO)_4$ | 2111 (27) | 2065 (41) | 2039 (65) | 2020 (100) |

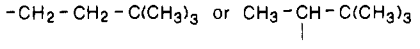
[a] Wavenumbers in cm$^{-1}$. [b] Relative intensities in parentheses; intensities in absorbance relative to $A$ = 100 of the most intense band.

**Table II.** Comparison of the Average C–O Stretching Frequencies of $RC(O)Co(CO)_4$ and $RC(O)Rh(CO)_4$ with the Corresponding Values of the Terminal $M_4(CO)_9$ Core of the $M_4(CO)_{12}$ Compounds[a]

| compd | M = Co; $R = -C_2H_5$ | M = Rh; $R = -(C_2H_4)C(CH_3)_3$ |
|---|---|---|
| $RCOM(CO)_4$ | 2047.1[b] | 2058.9 |
| $M_4(CO)_9$[c] | 2046.8 | 2057.7 |

[a] Frequencies in cm$^{-1}$. Doubly degenerate frequencies count twice. [b] Reference 7. [c] Reference 20.

The group R, since it derives from the olefin used, viz. 3,3-dimethyl-1-butene, may be either



$-CH_2-CH_2-C(CH_3)_3$ or $CH_3-CH-C(CH_3)_3$

or a mixture of both. High-pressure NMR studies are in progress in another laboratory to clarify this point of isomerism.[21]

Independently of this uncertainty, the correspondence between the characteristics of the spectra of the acylcobalt and acylrhodium compounds is perfect, including the general pattern of the spectrum and wavenumber distribution, as well as the relative intensities of the C–O bands (see Table I).

The final proof, of course, of the acylmetal type of this compound is the observation of the "organic" C–O stretching band of the acyl group. We succeeded in obtaining spectra of samples with low olefin-to-aldehyde conversions, where the aldehyde band at 1733 cm$^{-1}$ is still weak enough to allow the observation of the acyl band, expected at lower frequencies than the band of the aldehyde. In fact, the C–O frequency of the acyl group bonded to the $^{\bullet}Rh(CO)_4$ group appears at 1698 ± 3 cm$^{-1}$. This uncertainty in the wavenumber value is caused by the relative weakness of this band combined with the slight influence of the subsequent subtraction procedures upon this band position. The corresponding band of the propionylcobalt tetracarbonyl was observed[7] at 1720 cm$^{-1}$. For the time being, the question is open if this low-frequency shift of more than 20 cm$^{-1}$ is general for the $RC(O)Rh(CO)_4$ compounds or is related to the strongly branched R group.

The shift toward higher frequencies in the case of the rhodium compound relative to those of the cobalt analogue corresponds to the general trend in the carbonyls of the 3d versus 4d metals. In quantitative terms, the analogies are strikingly perfect: the average of the C—O stretching frequencies of the two acylmetal tetracarbonyls is shown in Table II in comparison with the averages of the terminal frequencies of both tetrametal dodecacarbonyls.[22]

An independent confirmation of the identity of the rhodium compound by direct synthesis is not possible owing to its extreme lability. Whereas the $RC(O)Co(CO)_4$ compounds could be handled relatively safely at room temperature and pressure, the acylrhodium tetracarbonyl compound rapidly decomposed in our closed circulation equipment as soon as the carbon monoxide partial pressure was reduced significantly below 20 bar at 25 °C.

Some comments are needed about the previously reported assignments of the C–O stretching bands observed at 2115, 2037, and 2019 cm$^{-1}$ to an alkyl- (specifically, ethyl-) rather to an acylrhodium tetracarbonyl.[11] These authors did, as a matter of fact, observe a fourth band in the same region at 2068 cm$^{-1}$; however, they attributed it to $Rh_4(CO)_{12}$. Moreover, a careful inspection of the two lower spectra shown in Figure 1 of the paper of King et al.[11] shows that there is a not insignificant spectral

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feature in those spectra at about 1700 cm$^{-1}$, in the low-energy wing of the aldehyde band, which these authors did not comment on. In our view, at least a part of this absorption can be assigned to the acyl band.

We believe, that in spite of calibration differences and differences in the nature of the group R, the reaction conditions in the two studies were similar enough to allow the conclusion that these authors observed the same type of compound as we report here, viz. a propionylrhodium tetracarbonyl rather than the ethylrhodium compound.

As our spectra demonstrate, no trace of the bridging band of $Rh_4(CO)_{12}$ at 1886 cm$^{-1}$ is present (Figures 1 and 2), whereas the terminal band at 2065.5 cm$^{-1}$ (i) has a considerable intensity, corresponding to the pattern observed with the acylcobalt tetracarbonyl compounds and (ii) is clearly a *single* band of regular shape, whereas the band of $Rh_4(CO)_{12}$ in this region consists of a sharp doublet, with a separation of 5.4 cm$^{-1}$.[22]

Also, in the paper of King et al.[11] it seemed strange that, under the conditions used, no CO insertion took place. Our results and analysis of the spectra also show that in the case of rhodium carbonyls only the acyl derivative can be observed directly in catalytic experiments and the concentration of the alkyl derivative (as well as those of tricarbonyl species suggested frequently in studies on catalytic cycles) is below the limit of infrared detectability.

## Experimental Section

The hydroformylation reactions were carried out in a specially constructed high-pressure autoclave.[14] The autoclave was connected to a membrane pump and a high-pressure infrared cell containing single-crystal silicon windows. The *n*-hexane solution was continuously circulated from the high-pressure autoclave to the high-pressure infrared cell and back to the autoclave under isobaric and isothermal conditions.

**Spectra.** The spectra reported here were made on a Perkin-Elmer PE983G infrared spectrophotometer. Scanning conditions were scan mode of 4 and noise filter of 4, corresponding to a resolution of 3.5 cm$^{-1}$. Higher resolution was avoided to reduce noise level. This PE983G spectrophotometer was equipped with a Data Station Model 3600 computer for the manipulation of spectra. Infrared reference spectra of *n*-hexane, $Rh_4(CO)_{12}$, 3,3-dimethyl-1-butene, and carbon monoxide dissolved in *n*-hexane were subtracted from the high-pressure in situ spectra of the hydroformylation solution by means of the software package included with the PE983G spectrophotometer.

**Chemicals.** All solutions were prepared by using standard Schlenk techniques under nitrogen. *n*-Hexane (Fluka, Purum) was distilled from Na/K under nitrogen. 3,3-Dimethyl-1-butene (Fluka, Puriss) was dried and stored over 4-Å molecular sieves. Carbon monoxide was prepared from the catalytic dehydration of formic acid (ETH-Z), and hydrogen was supplied by Pan Gas, Luzern. $Rh_4(CO)_{12}$ showed no $Rh_6(CO)_{16}$ impurities.

**Acknowledgment.** This work was supported by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung. Fruitful discussions with Professor P. Pino and Dr. I. T. Horváth are gratefully acknowledged.

**Note Added in Proof.** A reviewer suggested that the reaction should be repeated with ethylene as olefin. This has been performed in the meantime (conditions: $Rh_4(CO)_{12}$ 0.5 mM in *n*-hexane, 15 bar of ethylene, 2 bar of hydrogen, 40 bar of CO, at 25 °C). Again the formation of the corresponding *acyl* derivative, i.e. the propionylrhodium tetracarbonyl, was observed (IR bands at 2112, 2065, 2038, 2020, and 1696 cm$^{-1}$). Hydroformylation proceeds slowly under these conditions: the aldehyde CO band eventually appears at 1741 cm$^{-1}$.

With carbon monoxide pressure as low as 2–5 bar and only with ethylene but not with other olefins, an unknown species is formed (IR bands at 2089, 2039, and 2016 cm$^{-1}$) which upon increasing the CO pressure yields the same acylrhodium derivative as mentioned above. A detailed study of this species is in progress.

Upon exposure of the sample to air, the formation of the carboxylato-bridged dimeric compound $[Rh(CO)_2(\mu\text{-}C_2H_5CO_2)]_2$ reported in ref 10 could be observed ($\nu$(C–O) frequencies occur at 2095, 2073, 2043, and 2023 cm$^{-1}$).

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# First Examples of an Isomeric Methylene-Bridged Free Phosphano Phosphoranimine and a Metalated Phosphano Phosphoranimine. Synthesis, Characterization, and Isomerization of the Heterodifunctional Ligand $Me_3SiNPPh_2CH_2PPh_2$ and the Transmetalation to the Titanium Derivative $(\eta^5\text{-}C_5H_5)TiCl_2NPPh_2CH_2PPh_2$

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Bis(diphenylphosphino)methane (**1**) reacts cleanly with azidotrimethylsilane to give initially one isomeric form of the silylated monophosphazene $Me_3SiNPPh_2CH_2PPh_2$ (**2**). This new phosphano phosphoranimine undergoes a thermally induced isomerization to form three different isomeric forms as established by $^1H$, $^{31}P$, and $^{29}Si$ NMR spectroscopy. In solutions of $CH_3CN$ the mixture of isomers of **2** reverts to the single isomer through a remarkable isomerization process. **2** also reacts with $CpTiCl_3$ to give the first example of a metalated phosphoranimino phosphane, $(\eta^5\text{-}C_5H_5)TiCl_2NPPh_2CH_2PPh_2$ (**3**).

## Introduction

Increasing interest in the synthesis of heterodifunctional ligands because of their potential as backbones for a variety of catalytically active heterobimetallic compounds[1–9] prompted a search for main-group skeletons containing appropriate reactive sites of different types that would be capable of holding varied heterometallic (i.e., early–late transition metal) centers together. Herein we report the first example of a methylene bridged phosphane–phosphoranimine compound, $RNPPh_2CH_2PPh_2$ (**2**) (R = $SiMe_3$), and also the discovery of the thermally induced isomerization of

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