Observation of H$_2$ Oxidative Addition to Chlorocarbonylbis(triphenylphosphine)rhodium(I) Using Parahydrogen-Induced Polarization

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First synthesized in 1957, RhCl(CO)(PPh$_3$)$_2$ is one of the best known complexes of rhodium(I).[1] The complex forms readily from Wilkinson's catalyst, RhCl(PPh$_3$)$_3$, by CO addition or aldehyde decarbonylation.[2] It is known to photodissociate CO and has been found to function as a photocatalyst for benzene carbonylation.[3,4] However, in contrast with its Ir(I) analog, Vaska's complex, which possesses a rich oxidative addition chemistry,[5] RhCl(CO)(PPh$_3$)$_2$ shows more limited reactivity.[6] For example, whereas H$_2$ oxidative addition to Vaska's complex occurs readily and is strongly favored thermodynamically,[7] the corresponding reaction with RhCl(CO)(PPh$_3$)$_2$ has not been seen directly at all. Through the use of parahydrogen-induced polarization, we now describe the first explicit observation of H$_2$ oxidative addition to RhX(CO)(PPh$_3$)$_2$ (X = Cl (**1a**), Br (**1b**), I (**1c**)), leading to unexpected binuclear complex products while revealing significant lability of the initial H$_2$ adducts. Beginning in 1987, parahydrogen-induced polarization has been shown to give strongly enhanced hydride resonances of H$_2$ oxidative addition products,[8] and in recent work, extraordinary signal enhancements have been found for ^{13}C and ^{31}P product nuclei when used in conjunction with the INEPT+ pulse sequence.[9]

When a 1 mM solution of RhCl(CO)(PPh$_3$)$_2$ (**1a**) in C$_6$D$_6$ under 3 atm of para-enriched H$_2$ (p-H$_2$) is thawed rapidly, shaken, and introduced into the probe of a 400-MHz NMR spectrometer at 342 K, the spectrum shown in Figure 1a is obtained within 60 s. The spectrum shows two new resonances at δ –19.31 and –19.66 which are almost identical in shape and contain antiphase components. The separation between these resonances (in Hz) changes with field, yielding a constant $\Delta\delta$ of 0.35. The hydride signals decay rapidly until they are no longer visible after *ca.* 5 min, but they can be regenerated if the tube is removed from the spectrometer, shaken, and returned to the probe for observation. On decoupling of the ^{31}P nuclei of the phosphine ligands, the two hydride resonances become doublets of antiphase doublets (Figure 1b) with a larger coupling of 24.5 Hz (J_{RhH}) and a smaller coupling of –11 Hz (J_{HH}).[10] A ^{31}P{INEPT} spectrum of the system, acquired with concurrent decoupling of the phenyl ^{1}H region, exhibits a doublet (J_{RhP} = 118 Hz) of triplets (J_{PH} = 14.5 Hz) centered at δ 40, with the outer lines of each triplet having opposite phase and half the intensity of the central line as in Figure 1d.[11]
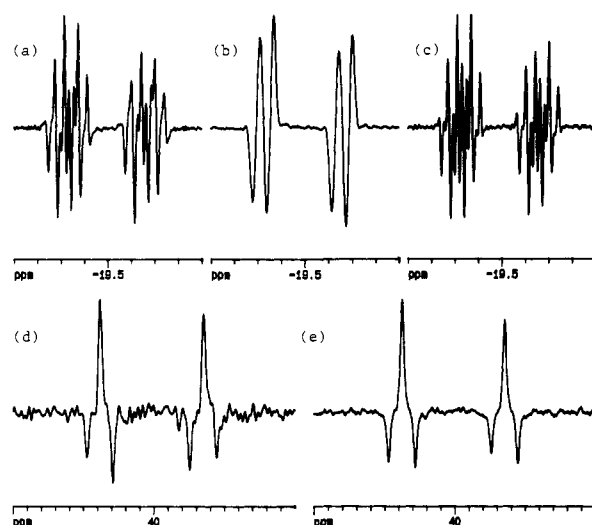

Figure 1. NMR spectra showing enhanced signals obtained for [H$_2$-Rh(PPh$_3$)$_2$(μ-Cl)$_2$Rh(PPh$_3$)CO] (**3a**), produced via eq 1 in benzene-d_6 at 342 K. The antiphase components arise across transitions separated by H–H coupling between the protons which were correlated in parahydrogen. (a) ^{1}H spectrum of **3a**; (b) ^{1}H{^{31}P} spectrum of **3a**; (c) ^{1}H spectrum of eq 1 using ^{13}CO-labeled **1a**; (d) ^{31}P{INEPT} spectrum of **3a**; (e) ^{31}P{INEPT} spectrum of eq 1 using ^{13}CO-labeled **1a**.

Importantly, when the H$_2$ addition reaction is performed using ^{13}CO-labeled **1a**, *no* ^{13}C coupling is observed and the spectra are identical to those obtained from unlabeled complex (Figure 1c and e).[11] The NMR results thus reveal that H$_2$ addition to **1a** has occurred but that based on (a) the absence of ^{13}C coupling when **1a**-^{13}CO is used, (b) the similarity of hydride chemical shifts in the product, and (c) the magnitude of J_{HH} which precludes a dihydrogen complex, the species observed is not the simple oxidative addition product RhH$_2$Cl(CO)(PPh$_3$)$_2$.

Parallel results were obtained with the bromo and iodo analogs, yielding polarized hydride signals at δ –18.36 and –18.39 for **1b** and at δ –16.36 and –16.73 for **1c**.[12] Again the similarity of the hydride chemical shifts of each product was inconsistent with the expected structure having one hydride trans to the halide and the other trans to CO. Although qualitative, the magnitude of the polarization in these experiments was in the order **1c** > **1b** > **1a**, consistent with the reactivity order I > Br > Cl for H$_2$ oxidative addition reported for the corresponding Ir(I) systems IrX(CO)-(PPh$_3$)$_2$.[13] In light of the absence of ^{13}C coupling when **1a**-^{13}CO was reacted with p-H$_2$, the same reaction with the dimer [Rh-(μ-Cl)(PPh$_3$)$_2$]$_2$ was examined. The ^{1}H NMR spectrum showed the formation of the Rh(III)/Rh(I) binuclear dihydride [H$_2$-Rh(PPh$_3$)$_2$(μ-Cl)$_2$Rh(PPh$_3$)$_2$] (**2**), originally identified by Tolman *without polarization*, and the H$_2$ adduct of Wilkinson's catalyst RhH$_2$Cl(PPh$_3$)$_3$ with polarized hydrides as previously reported by Weitekamp.[14,15] However, when the reaction of [Rh(μ-Cl)-

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(10) The absolute sign of the J_{HH} is obtained by comparing the emission/absorption characteristics of the hydride resonances observed for [H$_2$Rh-(PPh$_3$)$_2$(μ-Cl)$_2$Rh(PPh$_3$)CO] with those obtained for IrH$_2$Cl(CO)(PPh$_3$)$_2$.

(11) Professor Alex Bain (McMaster University) suggested using 45° excitation pulses to achieve maximum polarization transfer using the INEPT pulse sequence. The ^{31}P spectra were acquired using this modification, whereas much weaker signals were observed using INEPT with classical 90° excitation pulses.
(12) Selected spectral data for products of eq 1: **3a**, ^{1}H NMR (C$_6$D$_6$) δ –19.31 (m, J_{HH} = –11, J_{RhH} = 24.7, and J_{PH} = 16.3 Hz), –19.66 (m, J_{HH} = –11, J_{RhH} = 24.6, and J_{PH} = 14.5 Hz), ^{31}P{^{1}H-partial} δ 40.01 (dt, J_{RhH} = 118 and J_{PH} = 14.5 Hz); **3b**, ^{1}H NMR (C$_6$D$_6$) δ –18.36 (m, J_{HH} = –10, J_{RhH} = 23.8, and J_{PH} = 14.7 Hz), –18.39 (m, J_{HH} = –10, J_{RhH} = 23.7, and J_{PH} = 12.5 Hz), ^{31}P{^{1}H-partial} δ 40.09 (dt, J_{RhH} = 117 and J_{PH} = 14 Hz); **3c**, ^{1}H NMR (C$_6$D$_6$) δ –16.36 (m, J_{HH} = –9, J_{RhP} = 23.3, and J_{PH} = 14.7 Hz), –16.73 (m, J_{HH} = –9, J_{RhP} = 23.2, and J_{PH} = 12.3 Hz), ^{31}P{^{1}H-partial} δ 39.6 (dt, J_{PH} = 16 and J_{RhP} = 117 Hz).
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$(PPh_3)_2]_2$ with p-H_2 was carried out at 352 K in the presence of 1-butanal, a good decarbonylation substrate and hence CO source, enhanced resonances identical to those in Figure 1a were observed.[16] Carbon monoxide thus appeared to be a necessary component of the H_2 oxidative addition product of **1**, despite the absence of any additional couplings when ^{13}CO-labeled **1a** was employed.

The key to understanding the nature of the product of **1** and p-H_2 lay in two additional experiments. Firstly, spectra recorded during the reaction of either $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ or Wilkinson's catalyst with p-H_2 in the presence of *cis*-2-hexene show two new polarized hydride resonances at δ -18.87 and δ -19.66 in addition to resonances for $RhH_2Cl(PPh_3)_3$ and $[H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh$-$(PPh_3)_2]$ (**2**). The two new resonances are coupled to each other and possess additional couplings to ^{103}Rh and ^{31}P (J_{RhH} = 22.2 and J_{HH} = -9.2 Hz) but have slightly different chemical shifts to those shown in Figure 1a.[17] Secondly, normal H_2 was reacted with a mixture of **1a** and $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ in benzene-d_6. In this case, Tolman's dihydride **2** was observed, as were additional unpolarized resonances at the same positions as those in Figure 1a. Upon repeating this reaction in CD_2Cl_2, the increase in solubility allowed ^{31}P{^{1}H} spectra to be recorded, showing the two resonances of **2** at δ 54.2 ($J_{Rh(I)P}$ = 194 Hz) and 37.6 ($J_{Rh(III)P}$ = 119 Hz) and two new resonances having analogous J_{RhP} at δ 52.2 ($J_{Rh(I)P}$ = 196 Hz) and 39.2 ($J_{Rh(III)P}$ = 119 Hz). These experiments, as well as all of the preceding observations, can be accommodated by the formation of a Rh(III)/Rh(I) binuclear dihydride $[H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)(CO)]$ (**3**) in the reaction of **1** with H_2 (eq 1). In **3** the C_2 symmetry of the dihydride
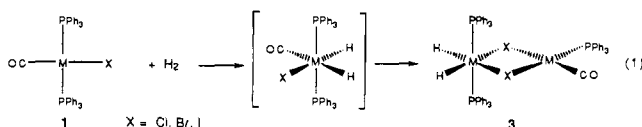
2 is removed by replacement of one PPh_3 of the Rh(I) center with CO, accounting for the inequivalence of the hydride resonances. For the reaction involving $RhCl(PPh_3)_3$ and *cis*-2-hexene, the olefin binds to the Rh(I) center in place of the CO ligand.

Strong support for this proposal comes from the reaction of p-H_2 with samples that contain mixtures of all three complexes **1a**, **1b**, and **1c**. The resulting ^{1}H{^{31}P} NMR spectra are more

complex than would be expected if only the three homohalide products **3a**, **3b**, and **3c** were formed. Specifically, the intensity of the two independent subsets of **3a** and **3b** at around δ -19.31 and -18.36 show significant intensity reductions relative to that expected for their partners at around δ -19.66 and -18.39, respectively. In fact, when an excess of **1c** is employed relative to **1b** and **1a**, the lower field resonances of **3a** and **3b** are completely suppressed and only weak signals are observed in the regions expected for those of their higher field counterparts. In this experiment, the largest peaks are observed in the region between δ -16.36 and -16.73 and are readily assignable to **3c**. However, this region also contains two additional weak resonances comparable in intensity to those seen in the higher field regions of **3a** and **3b**. On the basis of these results and the fact that metal-hydride chemical shifts depend on the ligand trans to hydride, we conclude that: (i) mixed halide complexes of type **3** are formed, (ii) the iodide complex **1c** reacts with H_2 more quickly than either **1a** or **1b**, and (iii) there is a definite stereochemical preference for iodide in one of the bridge positions which relates to the formation of **3**.

The loss of CO is an essential step in forming **3** and strongly suggests that the CO ligand in the initial oxidative addition product, $RhH_2X(CO)(PPh_3)_2$, is relatively labile. This view is supported by the fact that polarized hydride resonances assignable to $IrH_2Cl(PPh_3)_3$ grow in over 30 min when Vaska's complex, $IrCl(CO)(PPh_3)_2$, is warmed in the presence of PPh_3 and p-H_2 at 362 K. When $IrCl(CO)(PPh_3)_2$ and PPh_3 alone are warmed for the same time *before* introduction of p-H_2, the NMR observations are unchanged, indicating that PPh_3 substitution of CO occurs only *after* oxidative addition and not before. In both of these reactions, the polarized hydride resonances of IrH_2Cl-$(CO)(PPh_3)_2$ are detected immediately.

In summary, $RhX(CO)(PPh_3)_2$ (**1**) has been observed directly to react with H_2 for the first time. The dihydride complex $[H_2$-$Rh(PPh_3)_2(\mu\text{-}X)_2Rh(PPh_3)CO]$ (**3**; X = Cl, Br, I) is only detectable because of the increase in NMR sensitivity achieved by utilization of the non-Boltzman spin distribution of p-H_2. The results also indicate that H_2 oxidative additions to the d^8 Rh(I) complexes **1** yield octahedral d^6 six-coordinate adducts that are very labile with respect to CO loss and react further to form binuclear species.

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