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Communication

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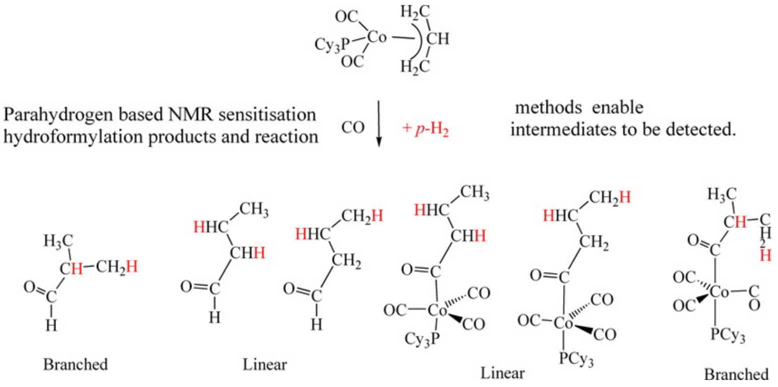

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Detection of Intermediates in Cobalt-Catalyzed Hydroformylation Using *para*-Hydrogen-Induced Polarization

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The cobalt-catalyzed hydroformylation of alkenes by $HCo(CO)_4$-based systems is of significant industrial importance.[1] When modified phosphine donors are included, improved linear to branched product ratios can be obtained.[2] Early studies by Heck and Breslow suggested aldehyde production occurs via a reaction sequence involving a monohydride precursor that ultimately yields a metal acyl intermediate which in turn eliminates the aldehyde after H_2 addition.[3] The detection and characterization of key species in this process has proven to be a complex process; examples of cobalt acyl and alkyl resting states have been isolated.[4]

We recently demonstrated the benefits of using allyl complexes as precursors in mechanistic NMR investigations of iridium-catalyzed hydroformylation reactions.[5] Here, we report on investigations using the cobalt-based allyl complex, $Co(\eta^3\text{-}C_3H_5)(CO)_2(PCy_3)$ **1**. We show that NMR spectroscopy, in conjunction with *para*-hydrogen,[6] provides direct evidence for each of the previously proposed steps in hydroformylation catalysis[3] and allows the detection of linear and branched cobalt acyl intermediates in addition to the corresponding aldehydes. These species are visible through the organic components of the ligands rather than the more usual hydride signals.

Complex **1** was obtained by the addition of 10 equiv of allylbromide to $Co(CO)_4Na$ at 273 K in THF, followed by the addition of 1 equiv of the phosphine at 295 K.[7,8] Crystals of **1** suitable for X-ray crystallography were obtained from toluene at room temperature. The structure of this complex, shown in Figure 1, is similar to that of the previously reported triphenylphosphine analogue[8] and corresponds to a piano-stool with a capping η^3-allyl ligand. NMR and IR data for **1** are provided in the Supporting Information.

When a d_8-toluene solution of **1** was placed under 3 atm of pure *para*-hydrogen (p-H_2) at 363 K and the reaction monitored by ^1H NMR spectroscopy, strong antiphase signals corresponding to the organic products, propene and propane, were observed. This confirms that **1** undergoes H_2 addition, either by losing a ligand or undergoing an $\eta^3-\eta^1$ allyl rearrangement, and that the resultant dihydride forms a propene hydride complex via transfer of a metal hydride to the allyl terminus, as shown in Scheme 1; such steps have been observed previously.[5,9] The observation of the p-H_2-enhanced NMR signals for propene, however, reveals that the $Co(CO)_2(PCy_3)(propene)(H)$ species undergoes reversible hydride−alkene insertions to place two hydrogen atoms from a single p-H_2 molecule into the alkene; the spectral features of the propene require exchange to incorporate p-H_2 into all of the available proton sites. The trapping of the corresponding cobalt alkyl intermediate with a second H_2 molecule and subsequent reductive elimination accounts for the enhanced propane resonances.

To confirm whether the hydride migration to the allyl terminus is reversible, a sample of **1** was placed under a 1:2 mixture of propene and p-H_2. ^1H NMR spectra recorded at 363 K then revealed enhanced signals for propane, but complex **1** was still rapidly consumed and the formation of the known complexes $Co(H)(CO)_3(PCy_3)$ and $Co(H)(CO)_2(PCy_3)_2$ indicated.[10] This suggests that $Co(CO)_2(PCy_3)(propene)(H)$ is unable to re-form the initial dihydride allyl complex.

Prior to examining the hydroformylation activity of **1**, a control experiment with CO was undertaken. $^{31}P\{^1H\}$ NMR spectroscopy

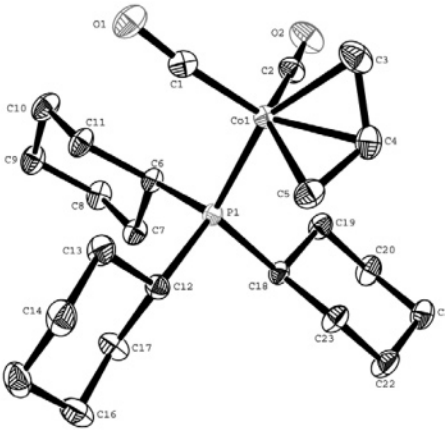
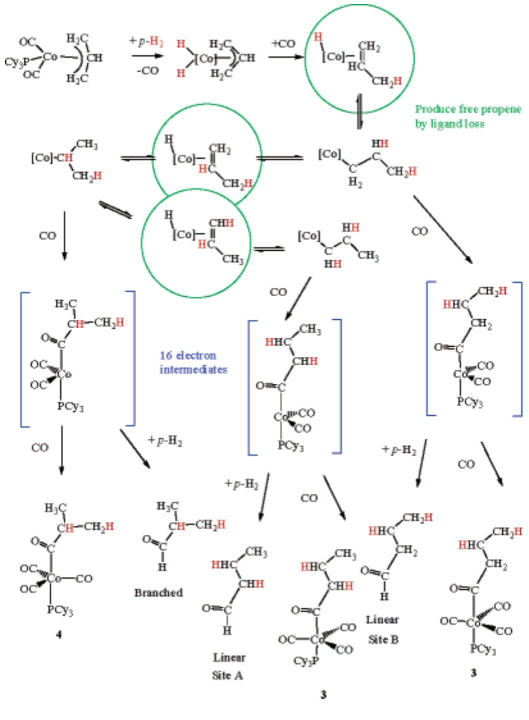


Figure 1. ORTEP diagram for $Co(\eta^3\text{-}C_3H_5)(CO)_2(PCy_3)$ **1**. Ellipsoids drawn at 50% probability level.

Scheme 1. Transformations Accounting for the p-H_2-Enhanced NMR Signals Seen for the Sites Where the Protons Appear in Red



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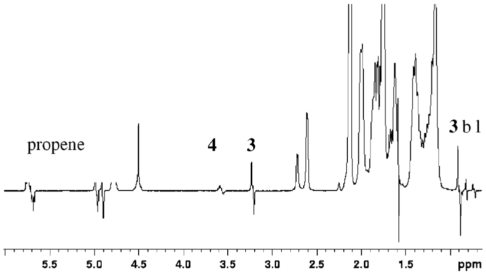

Figure 2. ^1H spectrum of a d_8-toluene solution containing **1** in the presence of CO and *p*-H_2 at 373 K with key resonances indicated (b = branched and l = linear aldehyde).

revealed the liberation of PCy_3, while the ^1H NMR spectrum confirmed the formation of a new η^3-allyl complex, which was subsequently identified as $Co(\eta_3\text{-}C_3H_5)(CO)_3$.[11] At 363 K, 15% of **1** was converted to $Co(\eta_3\text{-}C_3H_5)(CO)_3$.

When a d_8-toluene solution of **1** was placed under 3 atm of a 1:2 mixture of CO and H_2 at 363 K, the corresponding ^1H NMR spectrum showed much weaker *p*-H_2-enhanced signals for propene and propane. In addition, five new *p*-H_2-enhanced signals were also detected in clear regions of the spectrum at δ 3.57, 3.22, 0.92, 0.80, and 0.72 (Figure 2). The corresponding COSY spectrum connected the δ 3.22 signal (t, J_{HH} = 7 Hz) to the δ 0.92 (t, J_{HH} = 7 Hz) signal and a new resonance at δ 1.67 (sextet, J_{HH} = 8 Hz), which was masked by the phosphine. These data confirm that a linear $CH_2CH_2CH_3$ group has been formed with protons from *p*-H_2 being placed on all three of the carbon centers. When a $^1H\{^{31}P\}$ spectrum was recorded, the signal at δ 3.22 simplified due to removal of a single J_{PH} coupling of 3 Hz from a ^{31}P center which resonates at δ 62.0. COSY confirmed that the additional ^1H signal at δ 3.57 (septet, J_{HH} = 8 Hz) coupled to a signal at δ 1.20 (d, J_{HH} = 8 Hz), which indicated that a $CH(CH_3)_2$ group was formed. When this reaction was repeated with ^{13}CO, both of the terminal alkyl proton signals showed additional ^{13}C splittings that arose from ^{13}C signals that appeared at δ 235.6 and 240.9, respectively. Since both the latter resonances exhibited doublet multiplicities due to $^{31}P-^{13}C$ couplings (J_{PC} = 39.3 and 40.5 Hz, respectively), their origin as metal acyl groups, trans to a single phosphine ligand, was confirmed. The corresponding species are, therefore, $Co(COCH_2CH_2CH_3)(CO)_3(PCy_3)$ **3** and $Co(COCH(CH_3)_2)(CO)_3(PCy_3)$ **4**. In view of the fact that **3** and **4** contain PCy_3, it is possible to conclude that **1** reacts initially with H_2 via CO loss. The remaining *p*-H_2-enhanced resonances at δ 0.80 and 0.72 were shown to arise from the aldehydes $CH(O)CH(CH_3)_2$ and $CH(O)CH_2CH_2CH_3$, respectively.

The *p*-H_2-enhanced NMR signals of **3** and **4** can be accounted for by the reversible hydride transfer processes illustrated in Scheme 1; the signals seen for site B correspond to directly formed linear product, while those seen for site A arise via relinearized branched intermediates which can also react to give **4**.

When this reaction was observed at different temperatures using a constant concentration of **1** and a CO:H_2 ratio of 1:2, the size of the signals due to the aldehydes, propene, and propane increased with increase in temperature. Figure 3 summarizes these variations. A series of 1D EXSY experiments were then completed to test for magnetization transfer from **3** or **4** into the corresponding aldehydes. None was observable on the NMR time scale. The enhanced NMR signals seen for the two aldehydes, therefore, require the corresponding 16-electron intermediates, $Co(COCH_2CH_2CH_3)(CO)_2(PCy_3)$ and $Co(COCH(CH_3)_2)(CO)_2$ (PCy_3), to be trapped by H_2 (which leads to rapid aldehyde elimination) rather than CO (which leads to **3** or **4**). The variation in the observed product ratios reflects a higher linear aldehyde turnover at higher temperature.

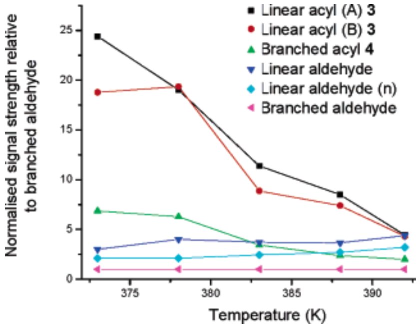

Figure 3. Plot of the relative *p*-H_2-based NMR signal intensities for species **3**, **4**, and the corresponding aldehydes as a function of temperature for samples of **1** reacting in toluene with 3 atm of a 2:1 mixture of CO and H_2. (Note, blue ♦ data obtained for a ^1H signal, measured using normal methods when the thermally polarized state was visible.)

These reactions were then repeated at 378 K, and the CO to H_2 ratio varied across the series 4:1, 1:1, 1:2, and 1:3. The relative strength of the NMR signals of **3** relative to those of **4** now proved to be minimized at a CO:H_2 ratio of 1:2; this also corresponded to the point of highest linear aldehyde selectivity.

Here, we have shown that the utilization of the PHIP effect allows the mapping of the hydroformylation reaction of a cobalt catalyst modified with PCy_3. The detection of reaction intermediates that do not contain a hydride ligand via enhanced signals within the organic ligand framework proved possible. In addition, the high signal strengths enable the hydroformylation products themselves to be monitored at very early reaction times. We expect this extension of the *para*-hydrogen approach to become applicable to the study of a wide range of catalytic reactions. We are currently using it to probe how the ligand sphere influences the reactions of modified and unmodified cobalt hydroformylation catalysts.

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Supporting Information Available: X-ray data for **1**, NMR data and experimental procedures (CIF, PDF). Crystal data for **1**: $C_{23}H_{38}CoO_2P$, FW 436.43, yellow blocks, crystal dimensions 0.32 × 0.24 × 0.14 mm, monoclinic, $P2_1/n$, $a = 10.4726(8)$ Å, $b = 15.4811(12)$ Å, $c = 13.8229(11)$ Å, $\beta = 92.511(2)°$, V = 2238.9(3) Å^3, $Z = 4$, μ(Mo Kα) = 0.853 mm^{-1}, $T = 115(2)$ K, 17 426 reflections collected, R(int) = 0.0247. This material is available free of charge via the Internet at http://pubs.acs.org.

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