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OXIDATIVE ADDITION OF RCOI TO $[AsPh_4][Rh(CO)_2I_2]$. SYNTHESIS OF $[AsPh_4][RCORh(CO)_2I_3]$ (R = Me, Et, n-Pr, i-Pr)*

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Abstract—Reaction of $[AsPh_4][Rh(CO)_2I_2]$ (**1**) with RCOI yields complexes $[AsPh_4]_2[RCORh(CO)I_3]_2$ (**2**, R = Me; **3**, R = Et; **4**, R = n-Pr; **5**, R = i-Pr). The ^{13}CO scrambling process for complexes $[AsPh_4][RCORh(^{13}CO)(S)I_3]$ (R = Me, Et; S = CD_3CN) along with the skeleton isomerization of $[AsPh_4][RCORh(CO)(S)I_3]$ (R = n-Pr, i-Pr) was determined by ^1H NMR spectroscopy. Rates of CO insertion into the Rh—C bond in $[AsPh_4][R—Rh(CO)_3I_3]$ (R = Me, n-Pr, i-Pr) were determined. Thermolysis of $[AsPh_4][MeCORh(CO)(CD_3CN)I_3]$ (**6**) in CD_3CN gives methyl iodide in contrast to $[AsPh_4][i\text{-}PrCORh(^{13}CO)(CD_3CN)I_3]$ (**7**) and $[AsPh_4][n\text{-}PrCORh(^{13}CO)(CD_3CN)I_3]$ (**8**) which give only propene as the organic fragment.

The rhodium-catalyzed HI-promoted carbonylation of alcohols is an industrially important process for the synthesis of carboxylic acids.[1] Key intermediates in this catalytic transformation are complexes with the structure $[RCORh(CO)_2I_3]^-$ which can be formed by either oxidative addition of alkyl iodides to $[Rh(CO)_2I_2]^-$[2] or by olefin insertion into $[H—Rh(CO)_2I_3]^-$.[3] While oxidative addition of methyl iodide has been extensively studied, the extension of this reaction to other alkyl iodides has not yet been reported. However, the reaction of ethylene with $[AsPh_4][H—Rh(CO)_2I_3]$ gives $[AsPh_4]_2[EtCORh(CO)I_3]_2$ (**3**) cleanly,[3] but attempts to use this procedure with α-olefins is problematic due to the formation of a mixture of regio isomers $[AsPh_4]_2[RCORh(CO)I_3]_2$ along with $[AsPh_4][Rh(CO)_2I_4]$. In this paper we describe a simple procedure to obtain a variety of complexes with the composition $[AsPh_4]_2[RCORh(CO)I_3]_2$ (**2**, R = Me; **3**, R = Et; **4**, R = n-Pr; **5**, R = i-Pr) by simple oxidative addition of acyl iodides to $[AsPh_4][Rh(CO)_2I_2]$ (**1**) along with their chemistry.

* Dedicated to Professor John E. Bercaw on the occasion of his 50th birthday.

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EXPERIMENTAL

General considerations

The NMR spectra were obtained on a GE Omega 500, Nicolet NT-300 wide-bore (300.75 MHz ^1H, 75.63 MHz ^{13}C) and GE Omega 300 narrow-bore (300 MHz ^1H) spectrometers. ^{13}C and ^1H chemical shifts are downfield from external Me_4Si. IR spectra were recorded on a Nicolet FT-IR spectrometer. The compounds $[Rh(CO)_2Cl]_2$,[5] $[Rh(C_2H_4)_2Cl]_2$,[5] $[AsPh_4]_2[CH_3(CO)Rh(CO)I_3]_2$[6] were prepared according to literature procedures. Acyl iodides were prepared according to literature procedures[7] from their respective acyl chlorides. ^{13}CO (99%) was purchased from Isotec Inc., 1,2-^{13}C-ethylene from MSD Isotopes and CCl_2FD (Freon 21) from Cambridge Isotope Laboratories. ^1H-NMR kinetics in the presence of CO were conducted in high pressure NMR tubes.[8]

$[AsPh_4][Rh(CO)_2I_2]$ (1)

Under an atmosphere of CO, 3 g (15.38 mmol) of $[Rh(CO)_2Cl]_2$ in 100 cm^3 of CH_3COOH were combined with 4.2 cm^3 (56.25 mmol) of HI. After stirring for 10 min at room temperature, 7.2 g (16.49 mmol) of $AsPh_4Cl \cdot H_2O$ dissolved in 50 cm^3 of

MeOH were added followed by 10 cm^3 of H_2O to induce the precipitation of the product. The solid was filtered, rinsed with H_2O and then dried under high vacuum. $[AsPh_4][Rh(CO)_2I_2]$ was isolated as yellow crystals. Yield 11.6 g (94.7%). ^{13}C-NMR (CD_2Cl_2): δ 184.2 (J_{Rh-C} = 72 Hz). Found: C, 39.11; H, 2.48; I, 32.21. Calc. for $C_{26}H_{20}AsI_2O_2Rh$: C, 39.23; H, 2.53; I, 31.88. IR (cm^{-1}, CD_2Cl_2): 2057 (vs); 1985 (vs).

$[AsPh_4][Rh(^{13}CO)_2I_2]$ (**1**-$(^{13}CO)_2$)

In the dry-box, 3 g (15.38 mmol) of $[Rh(C_2H_4)_2Cl]_2$ were dissolved in 30 cm^3 of Et_2O and the solution was transferred into a 50 cm^3 Fisher–Porter tube. Behind a barricade, the tube was charged with 60 psi ^{13}CO and the mixture stirred at 25°C for 15 min. At this point the pressure had dropped to 20 psi. The Fischer–Porter tube was recharged to 60 psi with ^{13}CO, this process repeated until ^{13}CO was no longer absorbed in the reaction. The tube was vented and the product was dissolved in 50 cm^3 of CH_2Cl_2, filtered and the solvent removed *in vacuo*. The dry residue was taken up in petroleum ether (30 cm^3). The solution was warmed to dissolve the complex and then cooled to −25°C for 1 h. The crystals were filtered, rinsed with petroleum ether and dried under vacuum. $[Rh(^{13}CO)_2Cl]_2$ was isolated as red crystals. Yield 2.4 g (80%). ^{13}C-NMR ($CDCl_3$): δ 177.6 (J_{Rh-C} = 76.8 Hz). Under an atmosphere of nitrogen, 3 g (15.30 mmol) of $[Rh(^{13}CO)_2Cl]_2$ in 100 cm^3 of CH_3COOH were allowed to react with 4.2 cm^3 (56.25 mmol) of HI and the solution stirred for 10 min at room temperature. A solution of 7.2 g (16.49 mmol) $AsPh_4Cl \cdot H_2O$ in 50 cm^3 of MeOH was added followed by 10 cm^3 H_2O to induce the precipitation of the product. The solids were filtered, rinsed with H_2O and dried under high vacuum. Yield 11.6 g (95%) of $[AsPh_4][Rh(^{13}CO)_2I_2]$. IR ($cm^{-1}$, CD_2Cl_2): 2007 (vs); 1939 (vs).

$[AsPh_4]_2[Et(CO)Rh(CO)I_3]_2$ (**3**)

A solution of 0.5 g (0.628 mmol) of $[Rh(CO)_2I_2][AsPh_4]$ in 20 cm^3 of CH_2Cl_2 cooled to −196°C was freeze–pump–thawed twice. At −196°C, 0.630 mmol of HI gas (previously purified by two freeze–pump–thaw cycles) and 1.9 mmol of ethylene were condensed. The frozen solution was slowly thawed to −80°C and then stirred for 30 min at that temperature. The solution was slowly warmed to room temperature. CH_2Cl_2 was removed *in vacuo*, leaving a reddish-brown solid. The solid was dissolved in 2 cm^3 of CH_2Cl_2 and the addition of *ca* 7 cm^3 of Et_2O caused a crystalline red–brown solid to precipitate from solution. The solid was filtered, rinsed with Et_2O and dried under vacuum. Yield 0.503 g (84%). Found: C, 35.14; H, 2.43; I, 41.27. Calc. for $C_{28}H_{25}AsI_3O_2Rh$: C, 35.32; H, 2.65; I, 39.99. IR (cm^{-1}, CD_2Cl_2): 2059 (vs); 1768 (m); 1701 (m). ^{1}H-NMR (CD_2Cl_2/60 psi CO): δ 0.98 (t, J = 7.1 Hz, 3H), 3.38 (q, J = 7.1 Hz, 2H).

$[AsPh_4]_2[Et(^{13}CO)Rh(^{13}CO)I_3]_2$ (**3**-$(^{13}CO)_2$)

The complex was prepared by the same method used for the non-labeled derivative but with $[AsPh_4][Rh(^{13}CO)_2I_2]$. The yield of **3**-$(^{13}CO)_2$ was 0.51 g (85.5%). IR (cm^{-1}, CD_2Cl_2): 2012 (vs); 1730 (m); 1666 (m). ^{13}C-NMR (CD_2Cl_2): δ 214.80 (J_{Rh-C} = 21.6 Hz), 208.51 (J_{Rh-C} = 23.1 Hz), 182.68 (J_{Rh-C} = 70.8 Hz), 182.38 (J_{Rh-C} = 66.7 Hz).

$[AsPh_4]_2[n\text{-}PrCORh(CO)I_3]_2$ (**4**)

In the dry-box a solution of 0.3 g (3.77 mmol) of $[AsPh_4][Rh(CO)_2I_2]$ in 30 cm^3 of CH_2Cl_2 was slowly reacted with 0.807 g (4.08 mmol) n-PrCOI and stirred for 15 min at room temperature. The solvent was removed *in vacuo* to *ca* 2 cm^3 and then *ca* 20 cm^3 of Et_2O were added to precipitate the product. The brown crystalline product was filtered, rinsed with Et_2O and dried under vacuum. Yield 0.33 g (90.6%). Found: C, 35.87; H, 2.68; I, 39.87. Calc. for $C_{29}H_{27}AsI_3O_2Rh$: C, 36.06; H, 2.82; I, 39.41. IR (cm^{-1}, CD_2Cl_2): 2059 (vs); 1985 (vs); 1749 (m); 1699 (m). ^{1}H-NMR (CD_2Cl_2/60 psi CO): δ 0.86 (t, J = 6.8 Hz, 3H), 1.55 (q, J = 6.8 Hz, 2H), 3.36 (t, J = 6.8 Hz, 2H).

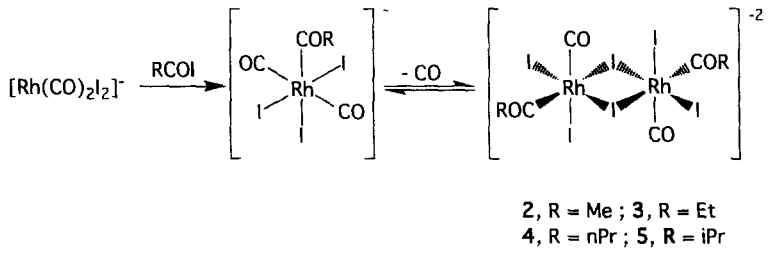
$[AsPh_4]_2[i\text{-}PrCORh(CO)I_3]_2$ (**5**)

The same procedure used to prepare $[AsPh_4]_2[n\text{-}PrCORh(CO)I_3]_2$ was followed. The reaction of $[AsPh_4][Rh(CO)_2I_2]$ (0.3 g, 3.77 mmol) with i-PrCOI (0.807 g, 4.08 mmol) yielded $[AsPh_4]_2[i\text{-}PrCORh(CO)I_3]_2$ (0.31 g, 85.1%). Found: C, 35.68; H, 2.58; I, 39.97. Calc. for $C_{29}H_{27}AsI_3O_2Rh$: C, 36.06; H, 2.82; I, 39.41. IR (cm^{-1}, CD_2Cl_2): 2056 (vs); 1985 (vs); 1749 (m); 1699 (m). ^{1}H-NMR (CD_2Cl_2/60 psi CO): δ 1.16 (d, J = 6.8 Hz, 6H), 3.37 (s, J = 6.8 Hz, 1H).

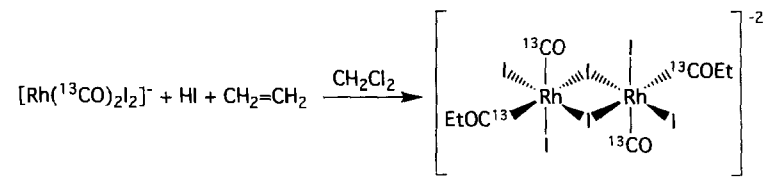
RESULTS AND DISCUSSION

From a synthetic point of view, complexes of composition $[AsPh_4][R(CO)Rh(CO)_2I_3]$ could be thought of as simple oxidative addition products in the reaction of RCOI with **1**. Indeed, we found that a variety of acyl iodides can be oxidatively added to **1** to provide a convenient entry into complexes

with the formula $[AsPh_4]_2[R(CO)Rh(CO)I_3]_2$. Reactions of RCOI, generated "in situ" by reacting the corresponding acyl chlorides with Me_3Si—I in dichloromethane,[7] with **1** gave $[AsPh_4][R(CO)Rh(CO)_2I_3]$ almost instantaneously at 25°C. $[AsPh_4][R(CO)Rh(CO)_2I_3]$ loses CO forming $[AsPh_4]_2[R(CO)Rh(CO)I_3]_2$ in high yield when the solvent is removed *in vacuo*. This transformation is totally reversible and one atmosphere of CO is sufficient to revert the dimeric structure back into $[AsPh_4][R(CO)Rh(CO)_2I_3]$.



2, R = Me ; **3**, R = Et
4, R = nPr ; **5**, R = iPr

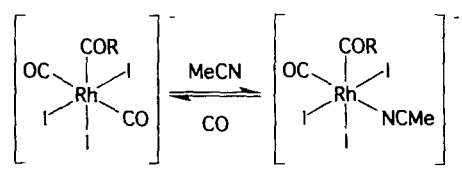


3

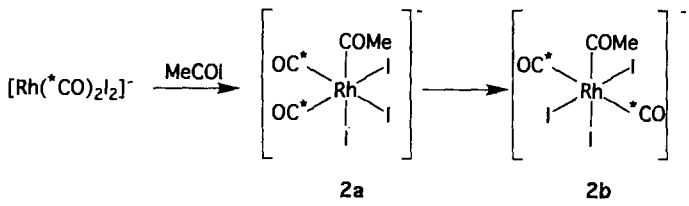
We believe that the solid state structure of **3** is similar to that reported for **2**.[9] The ^{1}H-NMR spectrum of **3** shows two methylene resonances at 3.66 and 3.54 ppm which suggests the presence of two isomers. The presence of two isomers is best observed in the ^{13}C-NMR spectrum of $[AsPh_4]_2[Et(CO)Rh(^{13}CO)I_3]_2$ that can be prepared analogously from **1**-$(^{13}CO)_2$ and EtCOI. At 25°C two carbonyl resonances {182.8 ppm [$^1J(^{103}Rh^{13}C)$ = 70.5Hz], 182.5 ppm [$^1J(^{103}Rh^{13}C)$ = 66.8Hz]} were observed. The relative proportion of these two isomers is temperature dependent as observed in the variable temperature ^{13}C-NMR. The doubly labeled complex **3**-$(^{13}CO)_2$ was also prepared as shown below. The ^{13}C-NMR spectrum shows in addition to the above mentioned CO resonances, two acyl resonances [215.9 ppm, $^1J(^{103}Rh^{13}C)$ = 21 Hz; 208.7 ppm, $^1J(^{103}Rh^{13}C)$ = 23 Hz)]. ^{13}C magnetization transfer experiments[10] at 25°C indicate that the two carbonyl resonances at 182.8 and 182.5 ppm are exchanging at a rate of about 0.1 s^{-1}. As expected the two acyl resonances at 215.9 and 208.7 ppm are also exchanging at that same rate. The carbonyl resonances and the acyl resonances do not exchange indicating that the CO deinsertion/insertion process is too slow to be measured by magnetization transfer techniques. Cleavage of the iodide bridges with ^{13}CO leaves in solution $[AsPh_4][Et(^{13}CO)Rh(^{13}CO)_2I_3]$ with only one acyl resonance [218.8 ppm, $^1J(^{103}Rh^{13}C)$ = 18.4 Hz] and only one carbonyl resonance [177.9 ppm, $^1J(^{103}Rh^{13}C)$ = 54 Hz].

A second method to generate monomeric complexes by breaking the iodide bridges consists of using polar solvents. In the presence of polar solvents, such as acetonitrile, the two isomers observed for **3**-$(^{13}CO)_2$ in the ^{13}C-NMR spectrum obtained in CD_2Cl_2 disappear and only one complex is observed [220.8 ppm, broad singlet; 184.9 ppm, $^1J(^{103}Rh^{13}C)$ = 21 Hz]. If the NMR spectrum is obtained in the presence of ^{13}CO it is possible to detect not only **1**-$(^{13}CO)_2$ but also $[AsPh_4][Et CORh(^{13}CO)(CD_3CN)I_3]$. As expected, the relative amounts of these two complexes will depend on the CO concentration in solution.

The reaction of acyl iodides with [As



Ph_4][Rh($^{13}CO)_2I_2$] was studied in detail by ^{13}C-NMR. When one equivalent of acetyl iodide is allowed to react with 1 equivalent of [$AsPh_4$][Rh($^{13}CO)_2I_2$] at $-80°C$ in CD_2Cl_2, no reaction was observed. Upon increasing the temperature from $-80°C$ to 25°C, a two step process is observed leading to the formation of [$AsPh_4$][Me(CO)Rh($^{13}CO)_2I_3$]. The assignment of structures **2a** and **2b** was based on low temperature ^{13}C NMR. For complex **2b**, the $-120°C$ (CD_2Cl_2/$CDFCl_2$, 1/1 v/v) ^{13}C spectrum shows an ABX system for the carbonyl ligands (X being rhodium) whereas in complex **2a**, they remain as a doublet. The restricted rotation of the acetyl ligand, due to steric hindrance with the iodide ligands, is presumably the cause of inequivalent CO ligands in complex **2b** (Fig. 1). The presence of CO does not inhibit the *cis–trans* isomerization, implying that CO dissociation is not required for isomerization. From microscopic reversibility the reductive elimination of acetyl iodide from **2** would require the isomerization to the *fac*-**2** isomer before acetyl iodide can be reductively eliminated.



In contrast to the reaction of [$AsPh_4$][H—Rh($CO)_2I_3$] with propene, which gives a mixture of acyl-complexes, reaction of n-PrCOI

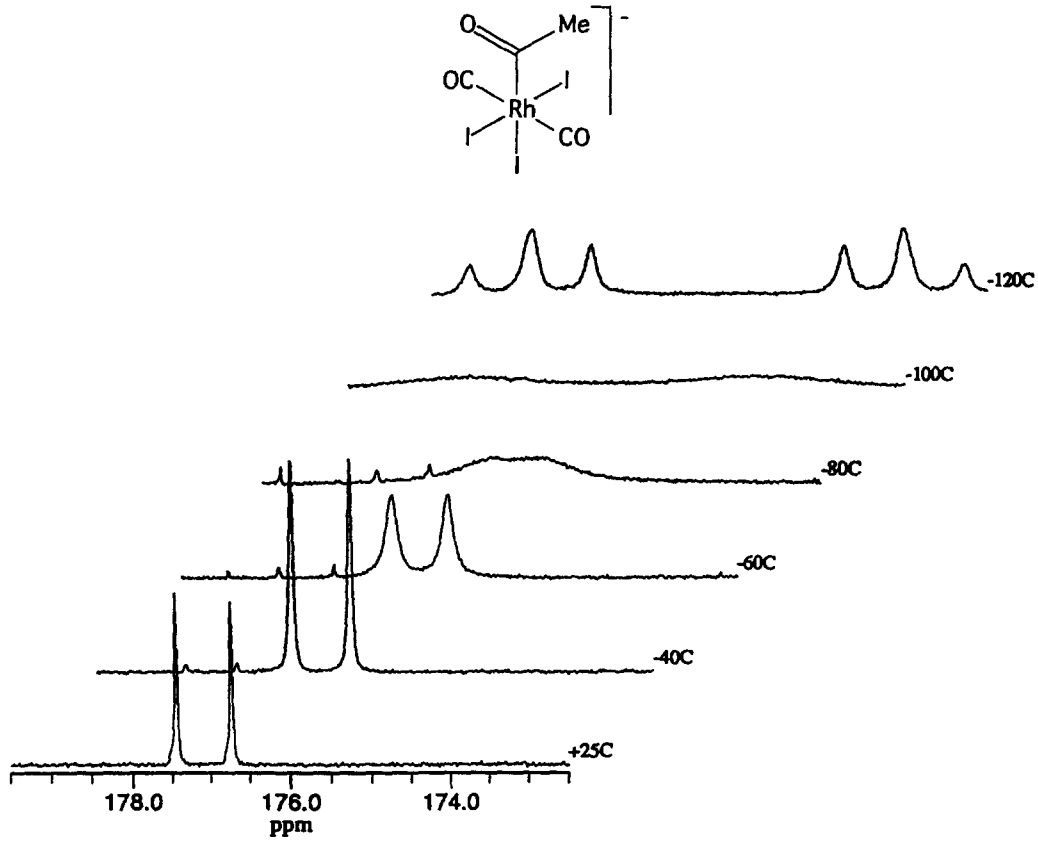


Fig. 1. Variable temperature ^{13}C-NMR of [$AsPh_4$][Me(CO)Rh($^{13}CO)_2I_3$] in CD_2Cl_2/$CDFCl_2$ under 60 psi ^{13}CO in the region of the carbonyl resonances.

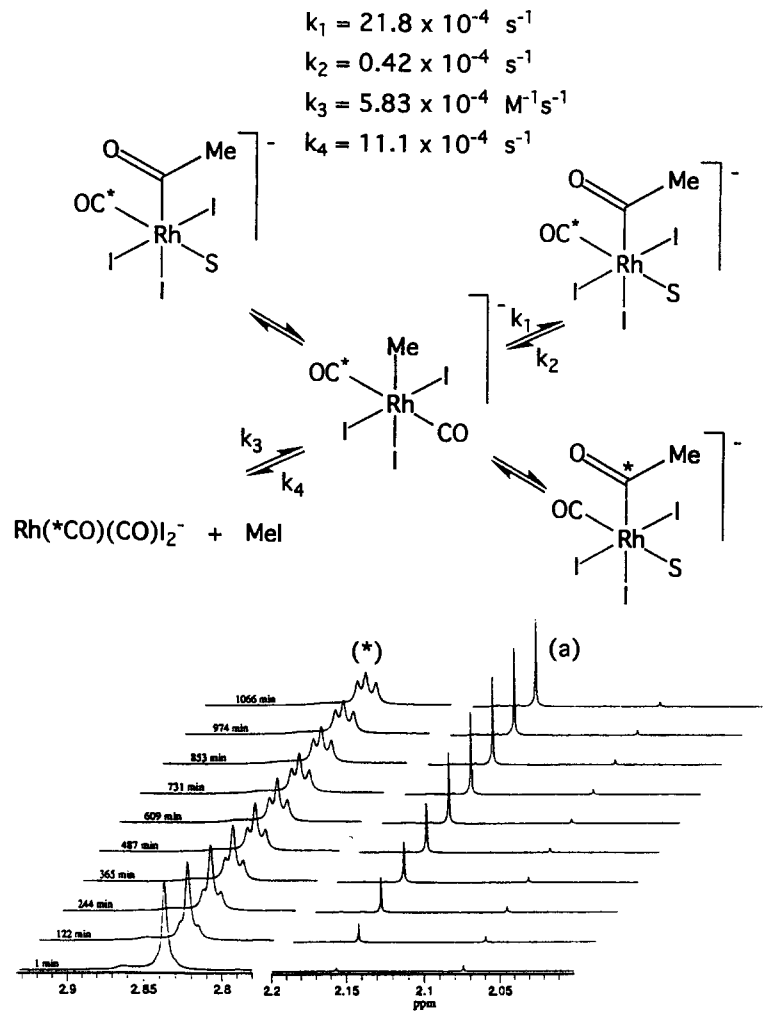


Fig. 2. Isomerization of $[AsPh_4][Me(CO)Rh(^{13}CO)(CD_3CN)I_3]$ into $[AsPh_4][Me(^{13}CO)Rh(CO)(CD_3CN)I_3]$ and decarbonylation to MeI at 60°C in CD_3CN. (a) = MeI, (*) = Me(CO)Rh, (**) = $Me(^{13}CO)Rh$.

and i-PrCOI with **1** gives only one product respectively. Attempts to recrystallize complexes **4** or **5** were unsuccessful due to the isomerization in solution to give an equilibrium mixture of **4**, **5** and presumably mixed dimers.

Previous work[11] attempting to detect the reversibility of CO insertion into Rh—C bonds has shown that $[AsPh_4]_2[Me(CO)Rh(^{13}CO)I_3]_2$ scrambles ^{13}CO into the acyl group to give $[AsPh_4]_2[Me(^{13}CO)Rh(CO)I_3]_2$ in dichloromethane solution at 35°C. The participation of structures such as **2** in catalysis is rather questionable due to the propensity of this type of binuclear complexes to give mononuclear complexes under very mild conditions in the presence of even weak donor ligands. Searching for reversible CO insertion chemistry, we observed a slow and clean ^{13}CO scrambling process when **2** is heated in $CDCl_3$ at 50°C in the presence of ^{13}CO. First a fast exchange with ^{13}CO to give $[AsPh_4][Me(CO)Rh(^{13}CO)_2I_3]$, then subsequent label scrambling into the acyl group was observed. Similarly, when **1**-$(^{13}CO)_2$ was treated with 3 equivalents of acetyl iodide and heated to 50°C in $CDCl_3$, we not only observed ^{13}CO scrambling into the acyl group in $[AsPh_4][Me(CO)Rh(CO)_2I_3]$ but we also detected $Me^{13}COI$. This observation led us to examine the reactivity of other acyl iodides, where in addition to ^{13}CO incorporation into the acyl group we could also test for isomerization of the alkyl chain. In the case of larger alkyl groups in addition to reductive elimination of alkyl iodides, β-hydrogen elimination could potentially compete to produce a mixture of regioisomers and/or a mixture of alkyl iodides and/or olefins.

The reaction of butyryl iodide with **1**-$(^{13}CO)_2$ was used to test the previous hypothesis. We observed that $[AsPh_4][n\text{-}Pr(CO)Rh(^{13}CO)_2I_3]$ $\{\delta\ ^{13}C = 178.02, [^1J(^{103}Rh^{13}C) = 54.2\ Hz]\}$, formed by

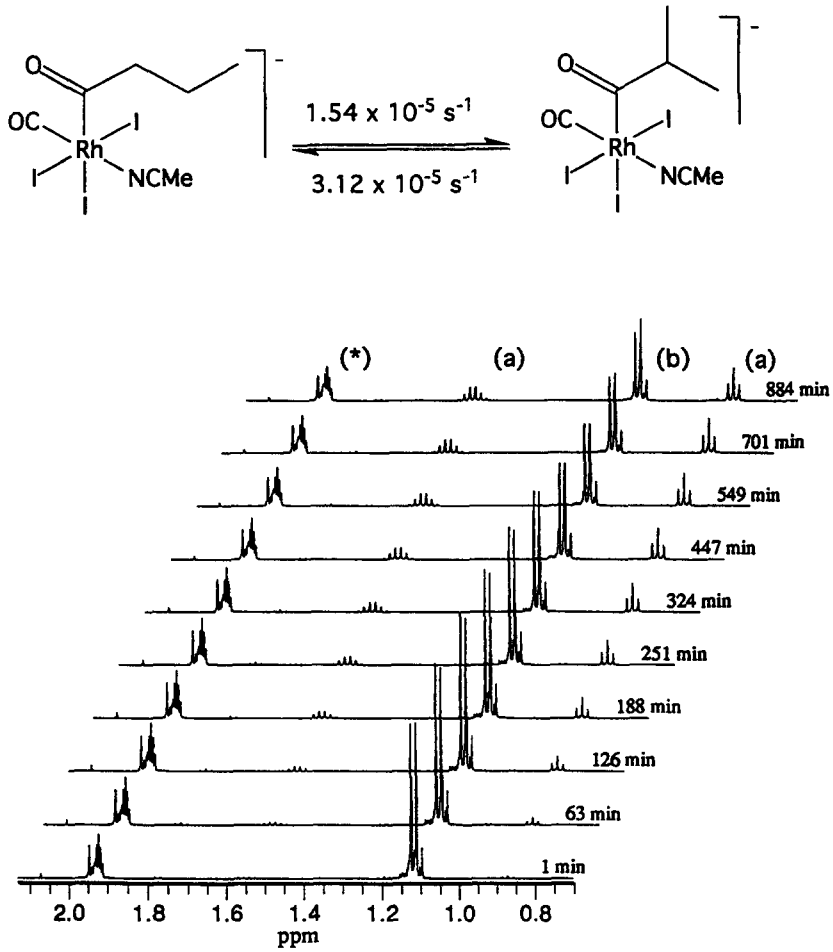


Fig. 3. Isomerization of $[AsPh_4][i\text{-}Pr(CO)Rh(CO)(CD_3CN)I_3]$ into $[AsPh_4][n\text{-}Pr(CO)Rh(CO)(CD_3CN)I_3]$ at 50°C in CD_3CN. (a) = $CH_3CH_2CH_2CORh$, (b) = $(CH_3)_2CHCORh$, (*) = CD_3CN.

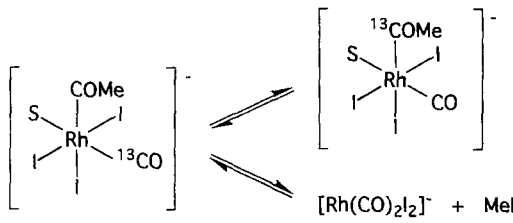
treatment of **1**-$(^{13}CO)_2$ with n-PrCOI, isomerized upon heating at 50°C for 16 h. The complexity of the ^{13}C- and ^1H-NMR at this stage in the reaction renders the characterization of the products difficult. However, the ^{13}C- and ^1H-NMR of the same reaction mixture in the presence of ^{13}CO (60 psi) are quite simple. In the presence of ^{13}CO, the ^{13}C-NMR shows the presence of only two rhodium-complexes: $[AsPh_4][n\text{-}Pr(^{13}CO)Rh(^{13}CO)_2I_3]$ δ 218.15 ppm [$^1J(^{103}Rh^{13}C)$ = 18.4 Hz], δ 178.02 ppm [$^1J(^{103}Rh^{13}C)$ = 54.2 Hz] and $[AsPh_4][i\text{-}Pr(^{13}CO)Rh(^{13}CO)_2I_3]$ δ 223.93 ppm [$^1J(^{103}Rh^{13}C)$ = 19.5 Hz], δ 178.15 ppm [$^1J(^{103}Rh^{13}C)$ = 54.3 Hz]. Analogous to the reaction with acetyl iodide, n-Pr^{13}COI and i-Pr^{13}COI were detected if excess n-PrCOI was used. In the case of larger alkyl groups the scrambling process is inhibited by CO. We were not able to detect scrambling of ^{13}CO into the acyl moiety of the rhodium complexes $[AsPh_4][RCORh(^{13}CO)_2I_3]$ in the case of R = Et, n-Pr, i-Pr in the presence of ^{13}CO (*ca* 60 psi) at 50°C. We observed only the elimination of RCOI and oxidation of **1** to $[AsPh_4][Rh(CO)_2I_4]$ promoted by the thermal decomposition of these rather unstable acyl iodides.

Furthermore, we found that isomerization of $[AsPh_4][MeCORh(^{13}CO)(S)I_3]$ into $[AsPh_4][Me\,^{13}CORh(CO)(S)I_3]$ and $[AsPh_4][i\text{-}PrCORh(CO)(S)I_3]$ into $[AsPh_4][n\text{-}PrCORh(CO)(S)I_3]$ (S = CD_3CN, DMF-d_7) proceeds smoothly at 50°C. The reactions can be conveniently monitored by ^1H-NMR kinetics (Figs. 2 and 3). The ^{13}CO scrambling in $[AsPh_4][MeCORh(^{13}CO)(S)I_3]$ is accompanied by the simultaneous formation of methyl iodide.

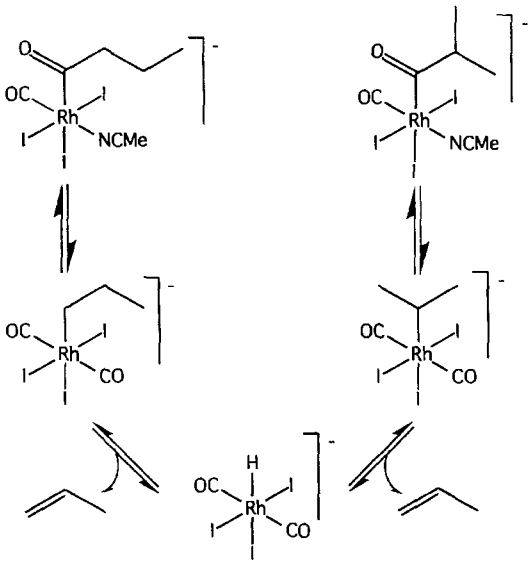
In contrast, the isomerization reaction of **7** or **8** gives only propene rather than n-propyl or i-propyl iodide as it might be expected by analogy to the case of methyl iodide carbonylation. The overall rate constants for the transformation were obtained from the first-order kinetic dependence as equilibrium was approached.

A plausible mechanism for this transformation involves the decarbonylation of $[AsPh_4][Me(CO)$

$Rh(^{13}CO)(S)I_3]$ into $[AsPh_4][MeRh(^{13}CO)(CO)I_3]$ that can either reinsert CO or ^{13}CO to give $[AsPh_4][MeRh(^{13}CO)(CO)I_3]$ or reductive eliminate MeI and $[AsPh_4][Rh(^{13}CO)(CO)I_2]$.



A completely analogous sequence of transformations can be proposed for the reversible isomerization of **7** into **8** as shown in Scheme 1. The



Scheme 1. Proposed mechanism for the reversible isomerization of $[AsPh_4][n\text{-}PrCORh(CO)(CD_3CN)I_3]$ into $[AsPh_4][i\text{-}PrCORh(CO)(CD_3CN)I_3]$ at 50°C in CD_3CN.

difference in this case is the formation of propene instead of n-propyl or i-propyl iodide if the reaction is carried out at higher temperatures. It appears that β-hydrogen elimination from $[AsPh_4][n\text{-}PrRh(CO)_2I_3]$ or $[AsPh_4][i\text{-}PrRh(CO)_2I_3]$ is faster than reductive elimination of n-PrI or i-PrI.

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