



OXIDATIVE ADDITION OF RCOI TO $[\text{AsPh}_4][\text{Rh}(\text{CO})_2\text{I}_2]$. SYNTHESIS OF $[\text{AsPh}_4][\text{RCORh}(\text{CO})_2\text{I}_3]$ ($\text{R} = \text{Me, Et, n-Pr, i-Pr}$)*

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Abstract—Reaction of $[\text{AsPh}_4][\text{Rh}(\text{CO})_2\text{I}_2]$ (**1**) with RCOI yields complexes $[\text{AsPh}_4][\text{RCORh}(\text{CO})\text{I}_3]$ (**2**, $\text{R} = \text{Me}$; **3**, $\text{R} = \text{Et}$; **4**, $\text{R} = \text{n-Pr}$; **5**, $\text{R} = \text{i-Pr}$). The ^{13}C O scrambling process for complexes $[\text{AsPh}_4][\text{RCORh}(\text{CO})(\text{S})\text{I}_3]$ ($\text{R} = \text{Me, Et}$; $\text{S} = \text{CD}_3\text{CN}$) along with the skeleton isomerization of $[\text{AsPh}_4][\text{RCORh}(\text{CO})(\text{S})\text{I}_3]$ ($\text{R} = \text{n-Pr, i-Pr}$) was determined by ^1H NMR spectroscopy. Rates of CO insertion into the Rh—C bond in $[\text{AsPh}_4][\text{R—Rh}(\text{CO})_3\text{I}_3]$ ($\text{R} = \text{Me, n-Pr, i-Pr}$) were determined. Thermolysis of $[\text{AsPh}_4][\text{MeCORh}(\text{CO})(\text{CD}_3\text{CN})\text{I}_3]$ (**6**) in CD_3CN gives methyl iodide in contrast to $[\text{AsPh}_4][\text{i-PrCORh}(\text{CO})(\text{CD}_3\text{CN})\text{I}_3]$ (**7**) and $[\text{AsPh}_4][\text{n-PrCORh}(\text{CO})(\text{CD}_3\text{CN})\text{I}_3]$ (**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 $[\text{RCORh}(\text{CO})_2\text{I}_3]^-$ which can be formed by either oxidative addition of alkyl iodides to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ or by olefin insertion into $[\text{H—Rh}(\text{CO})_2\text{I}_3]^-$.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 $[\text{AsPh}_4][\text{H—Rh}(\text{CO})_2\text{I}_3]$ gives $[\text{AsPh}_4][\text{EtCORh}(\text{CO})\text{I}_3]$ (**3**) cleanly,³ but attempts to use this procedure with α -olefins is problematic due to the formation of a mixture of regio isomers $[\text{AsPh}_4][\text{RCORh}(\text{CO})\text{I}_3]$ along with $[\text{AsPh}_4][\text{Rh}(\text{CO})_2\text{I}_4]$. In this paper we describe a simple procedure to obtain a variety of complexes with the composition $[\text{AsPh}_4][\text{RCORh}(\text{CO})\text{I}_3]$ (**2**, $\text{R} = \text{Me}$; **3**, $\text{R} = \text{Et}$; **4**, $\text{R} = \text{n-Pr}$; **5**, $\text{R} = \text{i-Pr}$) by simple oxidative addition of acyl iodides to $[\text{AsPh}_4][\text{Rh}(\text{CO})_2\text{I}_2]$ (**1**) along with their chemistry.

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 $[\text{Rh}(\text{CO})_2\text{Cl}]_2$,⁵ $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$,⁵ $[\text{AsPh}_4][\text{CH}_3(\text{CO})\text{Rh}(\text{CO})\text{I}_3]$ ⁶ were prepared according to literature procedures. Acyl iodides were prepared according to literature procedures⁷ 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

$[\text{AsPh}_4][\text{Rh}(\text{CO})_2\text{I}_2]$ (**1**)

Under an atmosphere of CO, 3 g (15.38 mmol) of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in 100 cm³ of CH_3COOH were combined with 4.2 cm³ (56.25 mmol) of HI. After stirring for 10 min at room temperature, 7.2 g (16.49 mmol) of $\text{AsPh}_4\text{Cl} \cdot \text{H}_2\text{O}$ dissolved in 50 cm³ of

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MeOH were added followed by 10 cm³ of H₂O to induce the precipitation of the product. The solid was filtered, rinsed with H₂O and then dried under high vacuum. [AsPh₄][Rh(CO)₂I₂] was isolated as yellow crystals. Yield 11.6 g (94.7%). ¹³C-NMR (CD₂Cl₂): δ 184.2 (*J*_{Rh-C} = 72 Hz). Found: C, 39.11; H, 2.48; I, 32.21. Calc. for C₂₆H₂₀AsI₂O₂Rh: C, 39.23; H, 2.53; I, 31.88. IR (cm⁻¹, CD₂Cl₂): 2057 (vs); 1985 (vs).

[AsPh₄][Rh(¹³CO)₂I₂] (1-(¹³CO)₂)

In the dry-box, 3 g (15.38 mmol) of [Rh(C₂H₄)₂Cl]₂ were dissolved in 30 cm³ of Et₂O and the solution was transferred into a 50 cm³ Fisher-Porter tube. Behind a barricade, the tube was charged with 60 psi ¹³CO 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 ¹³CO, this process repeated until ¹³CO was no longer absorbed in the reaction. The tube was vented and the product was dissolved in 50 cm³ of CH₂Cl₂, filtered and the solvent removed *in vacuo*. The dry residue was taken up in petroleum ether (30 cm³). 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(¹³CO)₂Cl]₂ was isolated as red crystals. Yield 2.4 g (80%). ¹³C-NMR (CDCl₃): δ 177.6 (*J*_{Rh-C} = 76.8 Hz). Under an atmosphere of nitrogen, 3 g (15.30 mmol) of [Rh(¹³CO)₂Cl]₂ in 100 cm³ of CH₃COOH were allowed to react with 4.2 cm³ (56.25 mmol) of HI and the solution stirred for 10 min at room temperature. A solution of 7.2 g (16.49 mmol) AsPh₄Cl·H₂O in 50 cm³ of MeOH was added followed by 10 cm³ H₂O to induce the precipitation of the product. The solids were filtered, rinsed with H₂O and dried under high vacuum. Yield 11.6 g (95%) of [AsPh₄][Rh(¹³CO)₂I₂]. IR (cm⁻¹, CD₂Cl₂): 2007 (vs); 1939 (vs).

[AsPh₄]₂[Et(CO)Rh(CO)I₃]₂ (3)

A solution of 0.5 g (0.628 mmol) of [Rh(CO)₂I₂][AsPh₄] in 20 cm³ of CH₂Cl₂ 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. CH₂Cl₂ was removed *in vacuo*, leaving a reddish-brown solid. The solid was dissolved in 2 cm³ of CH₂Cl₂ and the addition of *ca* 7 cm³ of Et₂O caused a crystalline red-brown solid to precipitate

from solution. The solid was filtered, rinsed with Et₂O and dried under vacuum. Yield 0.503 g (84%). Found: C, 35.14; H, 2.43; I, 41.27. Calc. for C₂₈H₂₅AsI₃O₂Rh: C, 35.32; H, 2.65; I, 39.99. IR (cm⁻¹, CD₂Cl₂): 2059 (vs); 1768 (m); 1701 (m). ¹H-NMR (CD₂Cl₂/60 psi CO): δ 0.98 (t, *J* = 7.1 Hz, 3H), 3.38 (q, *J* = 7.1 Hz, 2H).

[AsPh₄]₂[Et(¹³CO)Rh(¹³CO)I₃]₂ (3-(¹³CO)₂)

The complex was prepared by the same method used for the non-labeled derivative but with [AsPh₄][Rh(¹³CO)₂I₂]. The yield of 3-(¹³CO)₂ was 0.51 g (85.5%). IR (cm⁻¹, CD₂Cl₂): 2012 (vs); 1730 (m); 1666 (m). ¹³C-NMR (CD₂Cl₂): 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).

[AsPh₄]₂[n-PrCORh(CO)I₃]₂ (4)

In the dry-box a solution of 0.3 g (3.77 mmol) of [AsPh₄][Rh(CO)₂I₂] in 30 cm³ of CH₂Cl₂ 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 cm³ and then *ca* 20 cm³ of Et₂O were added to precipitate the product. The brown crystalline product was filtered, rinsed with Et₂O and dried under vacuum. Yield 0.33 g (90.6%). Found: C, 35.87; H, 2.68; I, 39.87. Calc. for C₂₉H₂₇AsI₃O₂Rh: C, 36.06; H, 2.82; I, 39.41. IR (cm⁻¹, CD₂Cl₂): 2059 (vs); 1985 (vs); 1749 (m); 1699 (m). ¹H-NMR (CD₂Cl₂/60 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).

[AsPh₄]₂[i-PrCORh(CO)I₃]₂ (5)

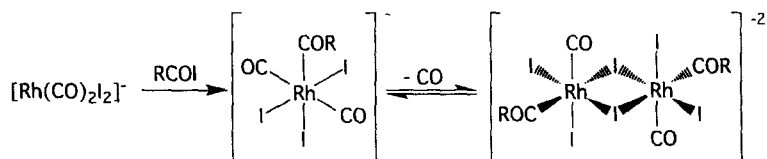
The same procedure used to prepare [AsPh₄]₂[n-PrCORh(CO)I₃]₂ was followed. The reaction of [AsPh₄][Rh(CO)₂I₂] (0.3 g, 3.77 mmol) with i-PrCOI (0.807 g, 4.08 mmol) yielded [AsPh₄]₂[i-PrCORh(CO)I₃]₂ (0.31 g, 85.1%). Found: C, 35.68; H, 2.58; I, 39.97. Calc. for C₂₉H₂₇AsI₃O₂Rh: C, 36.06; H, 2.82; I, 39.41. IR (cm⁻¹, CD₂Cl₂): 2056 (vs); 1985 (vs); 1749 (m); 1699 (m). ¹H-NMR (CD₂Cl₂/60 psi CO): δ 1.16 (d, *J* = 6.8 Hz, 6H), 3.37 (s, *J* = 6.8 Hz, 1H).

RESULTS AND DISCUSSION

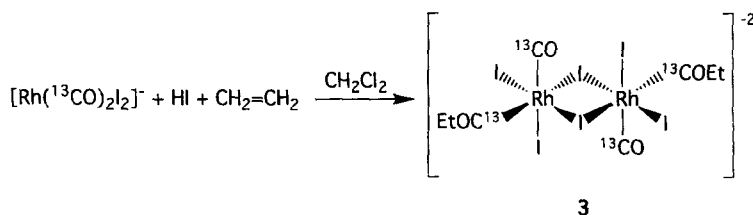
From a synthetic point of view, complexes of composition [AsPh₄][R(CO)Rh(CO)₂I₃] could be thought of as simple oxidative addition products in the reaction of RCOI with **1**. Indeed, we found that a variety of acyl iodides can be oxidatively added to **1** to provide a convenient entry into complexes

with the formula [AsPh₄]₂[R(CO)Rh(CO)I₃]₂. Reactions of RCOI, generated "in situ" by reacting the corresponding acyl chlorides with Me₃Si—I in dichloromethane,⁷ with **1** gave [AsPh₄][R(CO)Rh(CO)₂I₃] almost instantaneously at 25°C. [AsPh₄][R(CO)Rh(CO)₂I₃] loses CO forming [AsPh₄]₂[R(CO)Rh(CO)I₃]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 [AsPh₄][R(CO)Rh(CO)₂I₃].

ances 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 ¹³CO leaves in solution [AsPh₄][Et(¹³CO)Rh(¹³CO)₂I₃] with only one acyl resonance [218.8 ppm, ¹J(¹⁰³Rh¹³C) = 18.4 Hz] and only one carbonyl resonance [177.9 ppm, ¹J(¹⁰³Rh¹³C) = 54 Hz].



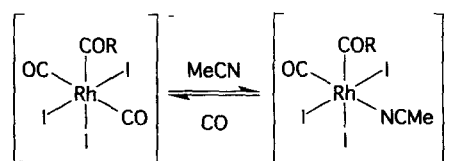
2, R = Me ; 3, R = Et
4, R = nPr ; 5, R = iPr



We believe that the solid state structure of **3** is similar to that reported for **2**.⁹ The ¹H-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 ¹³C-NMR spectrum of [AsPh₄]₂[Et(CO)Rh(¹³CO)I₃]₂ that can be prepared analogously from **1**-(¹³CO)₂ and EtCOI. At 25°C two carbonyl resonances {182.8 ppm [¹J(¹⁰³Rh¹³C) = 70.5 Hz], 182.5 ppm [¹J(¹⁰³Rh¹³C) = 66.8 Hz]} were observed. The relative proportion of these two isomers is temperature dependent as observed in the variable temperature ¹³C-NMR. The doubly labeled complex **3**-(¹³CO)₂ was also prepared as shown below. The ¹³C-NMR spectrum shows in addition to the above mentioned CO resonances, two acyl resonances [215.9 ppm, ¹J(¹⁰³Rh¹³C) = 21 Hz; 208.7 ppm, ¹J(¹⁰³Rh¹³C) = 23 Hz]. ¹³C magnetization transfer experiments¹⁰ 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 reson-

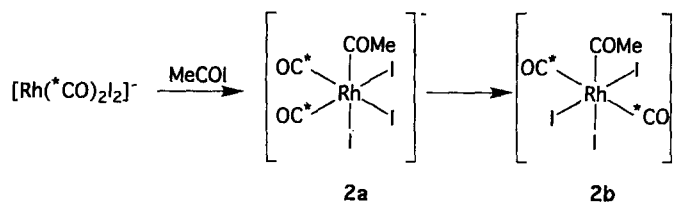
A second method to generate monomeric complexes by breaking the iodide bridges consists of using polar solvents. In the presence of polar solvents, such as acetonitrile, the two isomers observed for **3**-(¹³CO)₂ in the ¹³C-NMR spectrum obtained in CD₂Cl₂ disappear and only one complex is observed [220.8 ppm, broad singlet; 184.9 ppm, ¹J(¹⁰³Rh¹³C) = 21 Hz]. If the NMR spectrum is obtained in the presence of ¹³CO it is possible to detect not only **1**-(¹³CO)₂ but also [AsPh₄][EtCORh(¹³CO)(CD₃CN)I₃]. As expected, the relative amounts of these two complexes will depend on the CO concentration in solution.

The reaction of acyl iodides with [As



$\text{Ph}_4[\text{Rh}(^{13}\text{CO})_2\text{I}_2]$ was studied in detail by ^{13}C -NMR. When one equivalent of acetyl iodide is allowed to react with 1 equivalent of $[\text{AsPh}_4][\text{Rh}(^{13}\text{CO})_2\text{I}_2]$ 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 $[\text{AsPh}_4][\text{Me}(\text{CO})\text{Rh}(^{13}\text{CO})_2\text{I}_3]$. The assignment of structures **2a**

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



and **2b** was based on low temperature ^{13}C NMR. For complex **2b**, the -120°C ($\text{CD}_2\text{Cl}_2/\text{CDFCl}_2$, 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

fac-2 isomer before acetyl iodide can be reductively eliminated.

In contrast to the reaction of $[\text{AsPh}_4][\text{H}-\text{Rh}(\text{CO})_2\text{I}_3]$ with propene, which gives a mixture of acyl-complexes, reaction of *n*-PrCOI

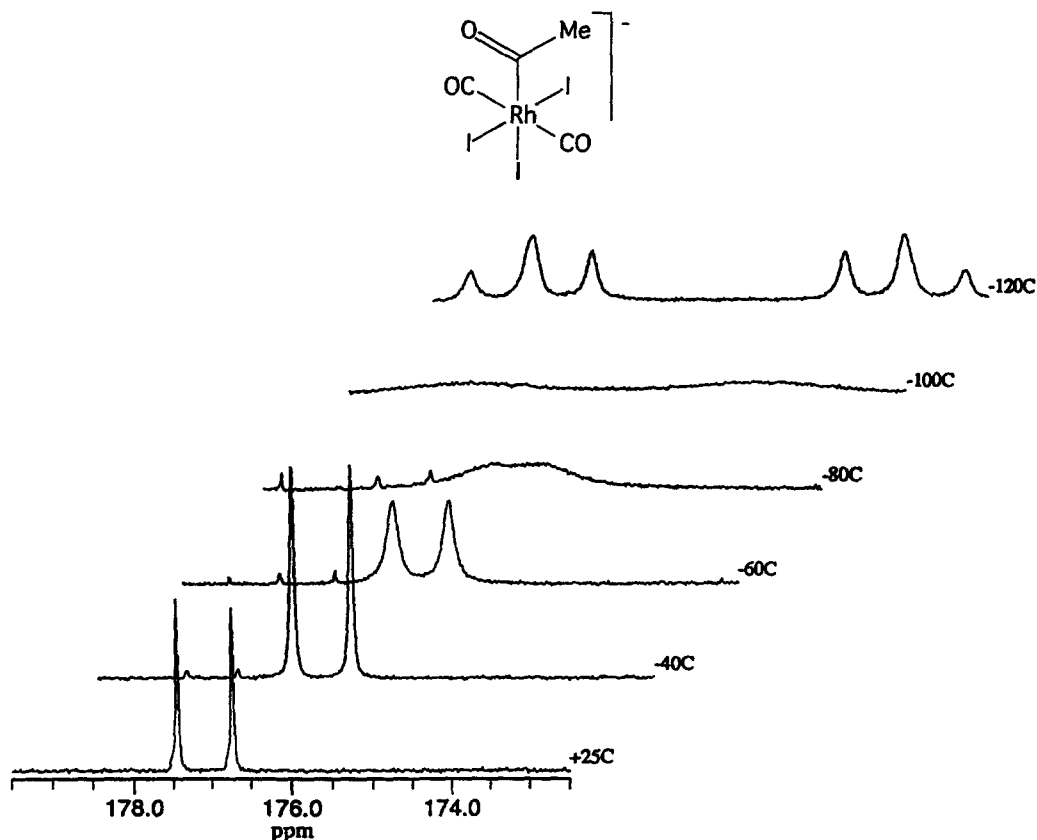


Fig. 1. Variable temperature ^{13}C -NMR of $[\text{AsPh}_4][\text{Me}(\text{CO})\text{Rh}(^{13}\text{CO})_2\text{I}_3]$ in $\text{CD}_2\text{Cl}_2/\text{CDFCl}_2$ under 60 psi ^{13}CO in the region of the carbonyl resonances.

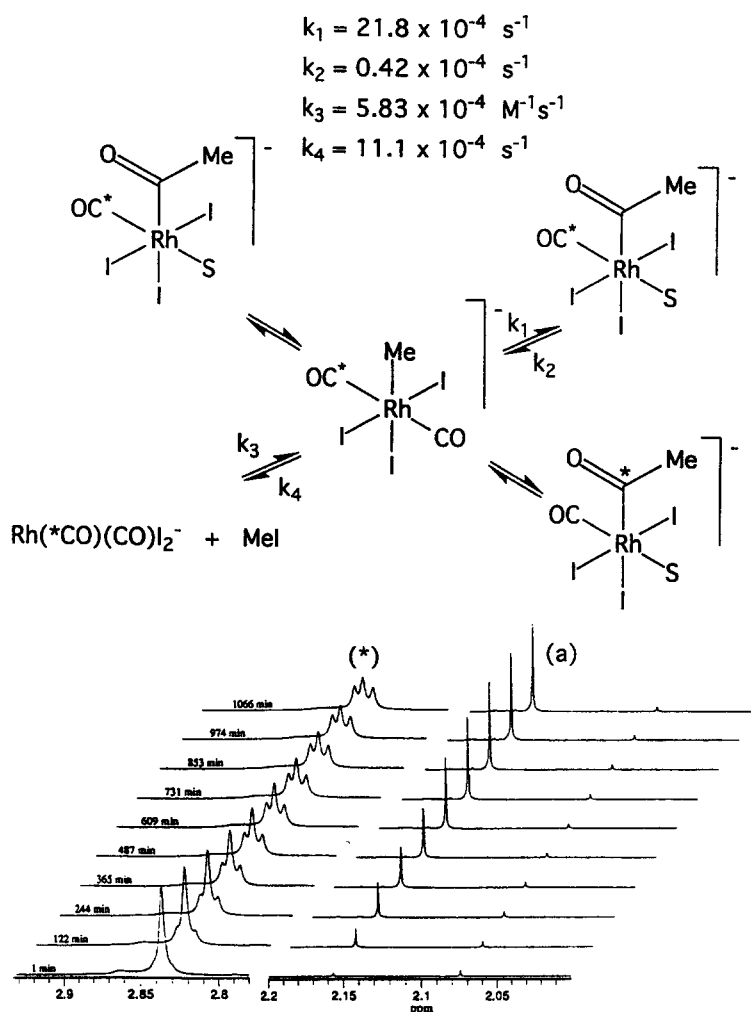


Fig. 2. Isomerization of $[\text{AsPh}_4][\text{Me}(\text{CO})\text{Rh}(\text{CO})(\text{CD}_3\text{CN})\text{I}_2]$ into $[\text{AsPh}_4][\text{Me}(\text{CO})\text{Rh}(\text{CO})(\text{CD}_3\text{CN})\text{I}_2]$ and decarbonylation to MeI at 60°C in CD_3CN . (a) = MeI, (*) = $\text{Me}(\text{CO})\text{Rh}$, (**) = $\text{Me}(\text{CO})\text{Rh}$.

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 work¹¹ attempting to detect the reversibility of CO insertion into Rh—C bonds has shown that $[\text{AsPh}_4]_2[\text{Me}(\text{CO})\text{Rh}(\text{CO})\text{I}_2]_2$ scrambles ^{13}CO into the acyl group to give $[\text{AsPh}_4]_2[\text{Me}(\text{CO})\text{Rh}(\text{CO})\text{I}_2]_2$ 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

$[\text{AsPh}_4][\text{Me}(\text{CO})\text{Rh}(\text{CO})_2\text{I}_2]$, then subsequent label scrambling into the acyl group was observed. Similarly, when **1**- $^{13}\text{CO}_2$ 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 $[\text{AsPh}_4][\text{Me}(\text{CO})\text{Rh}(\text{CO})_2\text{I}_2]$ 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**- $^{13}\text{CO}_2$ was used to test the previous hypothesis. We observed that $[\text{AsPh}_4][n\text{-Pr}(\text{CO})\text{Rh}(\text{CO})_2\text{I}_2]$ $\{\delta^{13}\text{C} = 178.02, [^1J(^{103}\text{Rh}^{13}\text{C}) = 54.2 \text{ Hz}]\}$, formed by

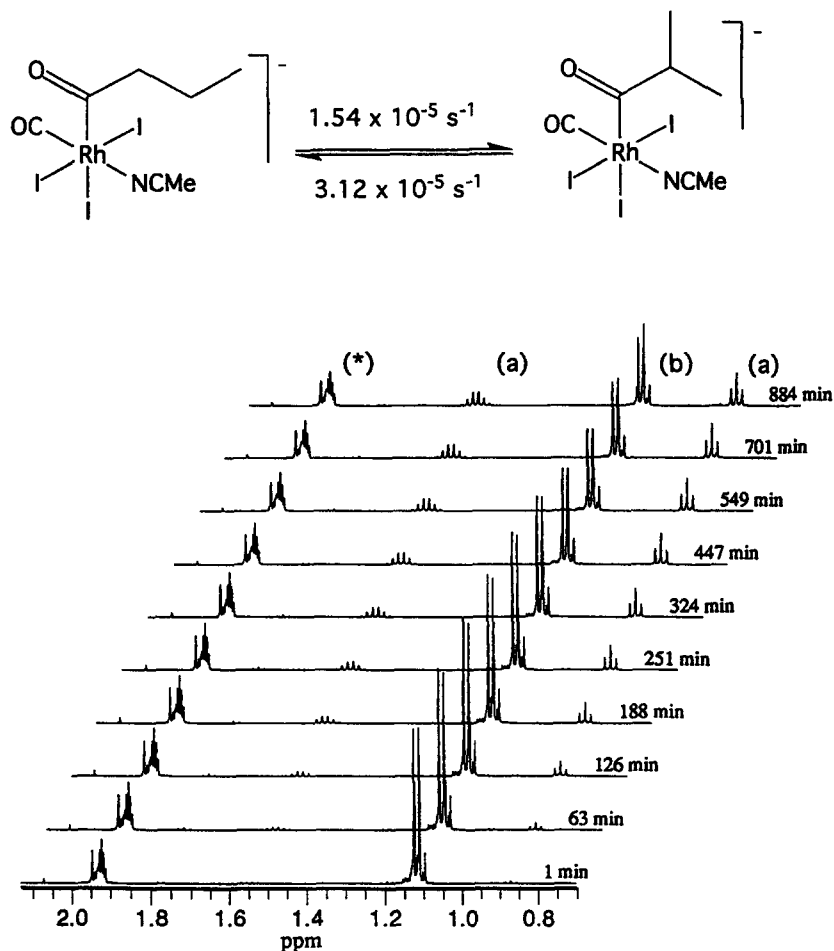


Fig. 3. Isomerization of $[\text{AsPh}_4][\text{i-Pr}(\text{CO})\text{Rh}(\text{CO})(\text{CD}_3\text{CN})\text{I}_3]$ into $[\text{AsPh}_4][\text{n-Pr}(\text{CO})\text{Rh}(\text{CO})(\text{CD}_3\text{CN})\text{I}_3]$ at 50°C in CD_3CN . (a) = $\text{CH}_3\text{CH}_2\text{CH}_2\text{CORh}$, (b) = $(\text{CH}_3)_2\text{CHCORh}$, (*) = CD_3CN .

treatment of **1**-(¹³CO)₂ with n-PrCOI, isomerized upon heating at 50°C for 16 h. The complexity of the ¹³C- and ¹H-NMR at this stage in the reaction renders the characterization of the products difficult. However, the ¹³C- and ¹H-NMR of the same reaction mixture in the presence of ¹³CO (60 psi) are quite simple. In the presence of ¹³CO, the ¹³C-NMR shows the presence of only two rhodium-complexes: $[\text{AsPh}_4][\text{n-Pr}(\text{CO})\text{Rh}(\text{CO})_2\text{I}_3]$ δ 218.15 ppm [¹*J*(¹⁰³Rh¹³C) = 18.4 Hz], δ 178.02 ppm [¹*J*(¹⁰³Rh¹³C) = 54.2 Hz] and $[\text{AsPh}_4][\text{i-Pr}(\text{CO})\text{Rh}(\text{CO})_2\text{I}_3]$ δ 223.93 ppm [¹*J*(¹⁰³Rh¹³C) = 19.5 Hz], δ 178.15 ppm [¹*J*(¹⁰³Rh¹³C) = 54.3 Hz]. Analogous to the reaction with acetyl iodide, n-Pr¹³COI and i-Pr¹³COI 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 ¹³CO into the acyl moiety of the rhodium complexes $[\text{AsPh}_4][\text{RCORh}(\text{CO})_2\text{I}_3]$ in the case of R = Et, n-Pr, i-Pr in the presence of ¹³CO (ca 60 psi) at 50°C. We observed only the elimination of RCOI

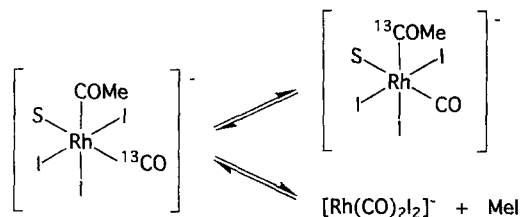
and oxidation of **1** to $[\text{AsPh}_4][\text{Rh}(\text{CO})_2\text{I}_4]$ promoted by the thermal decomposition of these rather unstable acyl iodides.

Furthermore, we found that isomerization of $[\text{AsPh}_4][\text{MeCORh}(\text{CO})(\text{S})\text{I}_3]$ into $[\text{AsPh}_4][\text{Me}^{13}\text{CORh}(\text{CO})(\text{S})\text{I}_3]$ and $[\text{AsPh}_4][\text{i-PrCORh}(\text{CO})(\text{S})\text{I}_3]$ into $[\text{AsPh}_4][\text{n-PrCORh}(\text{CO})(\text{S})\text{I}_3]$ (S = CD₃CN, DMF-*d*₇) proceeds smoothly at 50°C. The reactions can be conveniently monitored by ¹H-NMR kinetics (Figs. 2 and 3). The ¹³CO scrambling in $[\text{AsPh}_4][\text{MeCORh}(\text{CO})(\text{S})\text{I}_3]$ is accompanied by the simultaneous formation of methyl iodide.

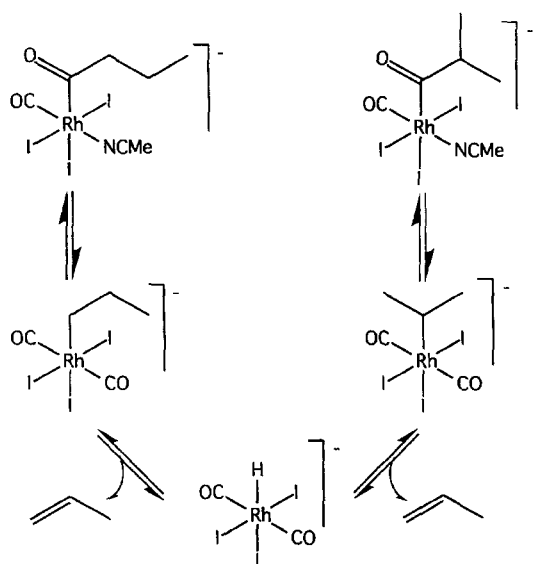
In contrast, the isomerization reaction of **7** or **8** gives only propene rather than n-propyl or i-propyl iodide as it might be expected by analogy to the case of methyl iodide carbonylation. The overall rate constants for the transformation were obtained from the first-order kinetic dependence as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

A plausible mechanism for this transformation involves the decarbonylation of $[\text{AsPh}_4][\text{Me}(\text{CO})$

$\text{Rh}(^{13}\text{CO})(\text{S})\text{I}_3]$ into $[\text{AsPh}_4][\text{MeRh}(^{13}\text{CO})(\text{CO})\text{I}_3]$ that can either reinsert CO or ^{13}CO to give $[\text{AsPh}_4][\text{MeRh}(^{13}\text{CO})(\text{CO})\text{I}_3]$ or reductive eliminate MeI and $[\text{AsPh}_4][\text{Rh}(^{13}\text{CO})(\text{CO})\text{I}_2]$.



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 $[\text{AsPh}_4][\text{n-PrCORh}(\text{CO})(\text{CD}_3\text{CN})\text{I}_3]$ into $[\text{AsPh}_4][\text{i-PrCORh}(\text{CO})(\text{CD}_3\text{CN})\text{I}_3]$ 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 $[\text{AsPh}_4][\text{n-PrRh}(\text{CO})_2\text{I}_3]$ or $[\text{AsPh}_4][\text{i-PrRh}(\text{CO})_2\text{I}_3]$ is faster than reductive elimination of n-PrI or i-PrI.

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