Identification of Rhodium−Rhenium Nonacarbonyl $RhRe(CO)_9$. Spectroscopic and Thermodynamic Aspects

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The hydrido metal carbonyl $HRe(CO)_5$ reacts rapidly with the cluster $Rh_4(CO)_{12}$ at room temperature in *n*-hexane solvent under CO and H_2 to give the coordinately saturated dinuclear carbonyl complex $RhRe(CO)_9$. At room temperature and low partial pressures of CO and H_2 (P_i < 2.2 MPa), an observable equilibrium is established between the reactants: $4HRe(CO)_5 + Rh_4(CO)_{12} + 4CO \rightarrow 4RhRe(CO)_9 + 2H_2$. This observation implies the facile activation of molecular hydrogen on $RhRe(CO)_9$ at mild conditions and in the presence of CO. A pure component spectrum of $RhRe(CO)_9$ was obtained by BTEM analysis from the in situ FTIR spectroscopic measurements of the equilibrated solutions. The new species has absorbance maxima at 1985.6(s), 2012.2(w), 2026.6(vs, br), 2075(s), and 2127.2(w) cm^{-1}, indicative of local trigonal bipyramidal geometry on the $-Rh(CO)_4$ moiety and square bipyramidal geometry on the $-Re(CO)_5$ moiety. Equilibrium measurements on the temperature interval T =289.7−308.2 K and the partial pressure intervals 0.2 MPa < P_{CO} < 2.2 MPa and 0.05 MPa < P_{H2} < 2.0 MPa were performed, providing an enthalpy of reaction $\Delta_r H = -116 \pm 29$ kJ/mol and entropy of reaction $\Delta_r S = -312 \pm 99$ J/(mol K). Attempts to isolate $RhRe(CO)_9$ by crystallization at −78 °C were unsuccessful.

Introduction

Metal carbonyl compounds have played a rather special historical role in the development of organometallic chemistry since they represent many of the first identified and isolated metal-organics and were used in many of the first detailed metal-organic mechanistic studies.[1] Mononuclear carbonyls of many of the transition metal elements have been synthesized. Additionally, many homometallic dinuclear and polynuclear carbonyl clusters have been synthesized.[2] Metal carbonyls are frequently used for stoichiometric as well as catalytic metal-mediated organic syntheses, to introduce organo-carbonyl functionalities.[3] In turn, carbonyl-containing functional groups are widely considered to be the backbone of many further synthetic strategies.[4]

Considerable interest in simple hetero-bimetallic metal carbonyls exists. Much of this interest arises from (a) outstanding structural questions, (b) the desire to further understand basic reaction mechanisms particularly where activation of small molecules occurs, and (c) the need to explain the observation of synergism in many bimetallic metal-mediated organic syntheses. Although a large variety of bimetallic polynuclear carbonyls have been synthesized and characterized, the same cannot be said of the most simple mixed-metal organometallics, namely, unsubstituted hetero-bimetallic dinuclear carbonyls. An extensive list of known unsubstituted hetero-bimetallic dinuclear carbonyls is provided in Table 1.

The species listed in Table 1 have a number of interesting attributes, but particular noteworthy are the nonisolatibility and reactivity under mild conditions of some of these species. For example, $CoRh(CO)_7$ is nonisolatable,[12] it readily reacts with molecular hydrogen at subambient temperatures,[14] and it initiates fairly

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Table 1. List of Known Unsubstituted Hetero-bimetallic Dinuclear Carbonyls and Relevant References to Their Characterization

species	refs for syntheses and character-ization	refs for thermo-dynamics	refs for mechanistic studies	refs for catalysis
$CoMn(CO)_9$	5	6	7	
$CoRe(CO)_9$	5b, 8	6		
$CoTc(CO)_9$	5b, 9			
$ReMn(CO)_{10}$	10	6	11	
$MnTc(CO)_{10}$	10b,10d			
$ReTc(CO)_{10}$	10b, 10d			
$CoRh(CO)_7$	12	13	14	14b, 15, 18
$CoRhCO)_8$	12b	13	14	14, 15
$RhRe(CO)_9$	this work	this work	this work	

rapid catalytic hydroformylation at ambient or even subambient temperatures at a total CO/H_2 pressure of 0.1 MPa.[15] These conditions are similar to those for the Wilkinson catalyst $HCORh(PPh_3)_3$.[16] The synergism observed in catalytic hydroformylation with $CoRh(CO)_7$ as precursor has been attributed to (a) facile hydrogen activation and subsequent generation of $HRh(CO)_3$/$HRh(CO)_4$ for the active rhodium cycle at low temperatures[17] and (b) cluster catalysis at high temperatures.[18] As noted previously, low temperature activation of molecular hydrogen is often very difficult to achieve particularly in the presence of carbon monoxide.[14,19]

Further, in the context of synergism, it can be mentioned that the existence of highly reactive hetero-bimetallic dinuclear carbonyls $MnRh(CO)_9$/$MnRh(CO)_8$ has been postulated in recent low-temperature hydroformylations where $HMn(CO)_5$ and $RCORh(CO)_4$ are simultaneously observed under catalytic reaction conditions. A new catalytic reaction topology, called bimetallic catalytic binuclear elimination, has been invoked to explain the kinetics. The active catalytic system consists of three sets of intermediates: mononuclear manganese, mononuclear rhodium, and hetero-bimetallic dinuclear species.[20]

In the present contribution the synthesis and characterization of the new hetero-bimetallic dinuclear carbonyl $RhRe(CO)_9$ is presented.

Experimental Section

General Information. All solution preparations and transfers were carried out under purified argon (99.9995%, Saxol, Singapore) atmosphere using standard Schlenk techniques.[21] The argon was further purified before use by passing it through a deoxy and zeolite column. Purified carbon monoxide (research grade, 99.97%, Saxol, Singapore) and purified hydrogen (99.9995%, Saxol, Singapore) were also further purified through deoxy and zeolite columns before they were used. Purified nitrogen (99.9995%, Saxol, Singapore) was used to purge the Perkin-Elmer FT-IR spectrometer system.

Table 2. Experimental Design

expt	step	P_{H2}, MPa	P_{CO}, MPa	$Rh_4(CO)_{12}$, mg	$HRe(CO)_5$, μL	hexane, mL	T, K
1	1	0.11	0.31	88.68	58	250	289.7
	2	0.21	0.31	88.68	58	250	289.7
	3	0.31	0.31	88.68	58	250	289.7
	4	0.51	0.31	88.68	58	250	289.7
2	1	0	2.0	77.87	70.0	250	298.3
	2	1.0	2.0	77.87	70.0	250	298.3
	3	2.0	2.0	77.87	70.0	250	298.3
3	1	0.05	0.2	83.86	70.0	250	298.3
	2	0.10	0.2	83.86	70.0	250	298.3
	3	0.15	0.2	83.86	70.0	250	298.3
	4	0.40	0.2	83.86	70.0	250	298.3
4	1	0.05	0.4	168.88	55.0	250	298.3
	2	0.10	0.4	168.88	55.0	250	298.3
	3	0.15	0.4	168.88	55.0	250	298.3
	4	0.20	0.4	168.88	55.0	250	298.3
	5	0.40	0.4	168.88	55.0	250	298.3
5	1	0.11	0.4	160.75	42.0	250	308.2
	2	0.21	0.4	160.75	42.0	250	308.2
	3	0.42	0.4	160.75	42.0	250	308.2
	4	0.80	0.4	160.75	42.0	250	308.2
	5	0.8	0.8	160.75	42.0	250	308.2
6	1	0.0	1.6	124.9	64.5	250	308.2
	2	1.0	1.6	124.9	64.5	250	308.2
	3	1.58	1.6	124.9	64.5	250	308.2
	4	2.0	1.6	124.9	64.5	250	308.2
	5	2.0	2.2	124.9	64.5	250	308.2

$Rh_4(CO)_{12}$ (98%) and $Re_2(CO)_{10}$ (99%) were purchased from Strem Chemicals (Newport, MA) and was used as obtained. $HRe(CO)_5$ was custom synthesized by Strem Chemicals.

Apparatus. In situ kinetic studies were performed in a 1.5 L stainless steel (SS316) autoclave (P_{max} = 22.5 MPa, Buchi-Uster, Swizerland), which is connected with a high-pressure infrared cell. The system is the same as that used previously.[22]

In Situ Spectroscopic Studies. An experimental design was planned, which would utilize the semibatch approach and algorithm.[23] All the experiments were performed in a similar manner. For example, first, single-beam background spectra of the IR sample chamber were recorded. Then 150 mL of *n*-hexane was transferred under argon to the autoclave. Under 0.2 MPa CO pressure, infrared spectra of the *n*-hexane in the high-pressure cell were recorded. The total system pressure was raised to the set CO pressure, and the stirrer and high-pressure membrane pump were started. After equilibration, infrared spectra of the CO/*n*-hexane solution in the high-pressure cell were recorded. A solution of $Rh_4(CO)_{12}$ dissolved in 50 mL of *n*-hexane was prepared, transferred to the high-pressure reservoir under argon, pressured with CO, and then added to the autoclave. After equilibration, infrared spectra of the $Rh_4(CO)_{12}$/CO/*n*-hexane/solution in the high-pressure cell were recorded. A solution of $HRe(CO)_5$ dissolved in 50 mL of *n*-hexane was prepared, transferred to the high-pressure reservoir under argon, pressured with CO, and then added to the autoclave. In the following steps, the semibatch experiment methodology was performed, namely, the CO/H_2 pressures were varied in each semibatch step. Once the system reached equilibrium, the CO/H_2 pressures were varied to conduct the next semibatch step. The detailed experimental design is shown in Table 2.

The experimental design of the experiments involved 250 mL of solvent and the intervals 289.7−308.2 K, P_{H2} = 0−2.0

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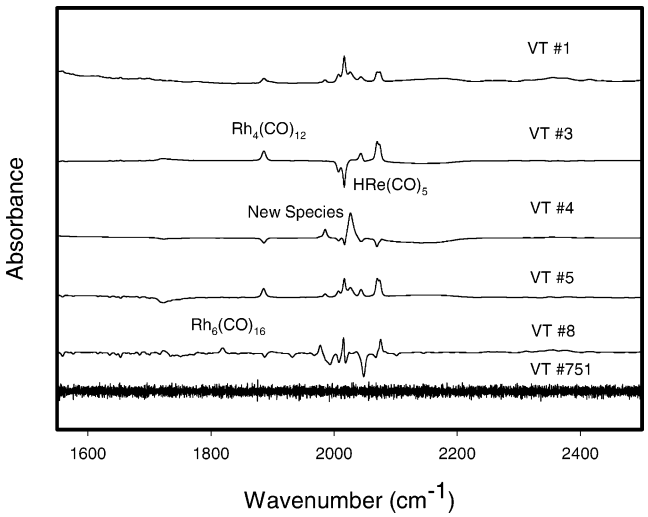

Figure 1. Singular value decomposition of the in situ spectroscopic data showing the first, third, fourth, and fifth significant vectors and the 751th vector. The marked extrema are those that were used to recover the organometallic pure component spectra by BTEM.

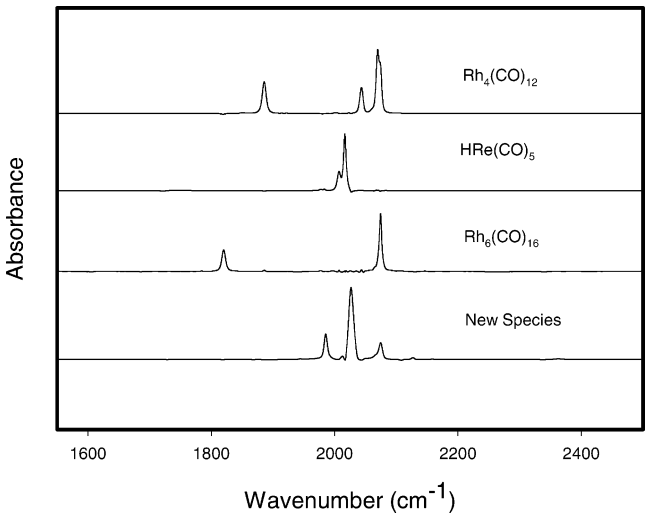

Figure 2. Recovered pure component spectra of the organometallic species using BTEM.

MPa, P_{CO} = 0.2−2.2 MPa, initial $Rh_4(CO)_{12}$ = 77.87−168.88 mg, and initial $HRe(CO)_5$ = 42.0−64.5 μL.

The in situ spectra were taken every 10 min in the range 1000−2500 cm^{-1} with a resolution of 4 cm^{-1}. Since equilibrium was normally established in hours, most of these spectra were recorded under nonequilibrium conditions. A total of 751 spectra were obtained for further spectroscopic analyses.

Attempt at Isolation/Crystallization. $HRe(CO)_5$ (40 μL) was reacted with 80.5 mg of $Rh_4(CO)_{12}$ at room temperature in 200 mL of *n*-hexane solvent under 2.0 MPa CO and in the absence of added H_2 for 6 h. The bright orange reaction mixture was then released to a 250 mL Schlenk tube and cooled with dry ice for 24 h under CO protection. Some orange solids were obtained after removing solvent/dissolved CO, and these were analyzed with FTIR. The spectra obtained are distinctly different than the solution spectrum of $RhRe(CO)_9$.

Results and Discussions

Spectral Analyses. BTEM was used to analyze the spectral data and obtain pure component spectra.[24] A total of 751 spectra were obtained in the experiments. Singular value decomposition (SVD) was employed first to decompose the experimental absorbance data matrix $\mathbf{A}_{751\times4751}$, without any preconditioning,[25] to give the orthonormal matrixes $\mathbf{U}_{751\times751}$ and $V^T_{4751\times4751}$.

The significant spectral extrema in the first few right singular vectors ($V^T_{751\times4751}$) were inspected and were used as targets in the BTEM algorithm. These noteworthy right singular vectors are presented in Figure 1. Four significant bands, as indicated by the numbers in Figure 1, are highlighted. These bands are prominent spectral features associated with the organometallics present and were targeted by BTEM.

The targeting of the highlighted bands in Figure 1 resulted in four pure component organometallic spectra. The reconstructed pure component spectra via BTEM are presented in Figure 2. These spectra were $Rh_4(CO)_{12}$, $HRe(CO)_5$, $Rh_6(CO)_{16}$, and a new species. The new species has peaks at 1985.6(s), 2012.2(w), 2026.6(vs, br), 2075(s), and 2127.2(w) cm^{-1}. Exhaustive use of BTEM on the remaining features in Figure 1 did not result in the recovery of any additional organometallic spectra.

Since the IR spectrum of the new species has no features indicating bridging C−O groups, a higher nuclearity cluster involving two or more Rh atoms is unlikely. Indeed, all known mixed Rh−M clusters having two or more Rh atoms have bridging carbonyls. Good examples include $Co_2Rh_2(CO)_{12}$, $CoRh_3(CO)_{12}$, $Rh_2Ir_2(CO)_{12}$, and $Rh_3Ir(CO)_{12}$.[14,26] Consequently, a low-nuclearity mixed rhodium and rhenium carbonyl is suspected. The simplest example would be a dinuclear complex with a single metal−metal bond and coordinatively saturated moieties $-Rh(CO)_4$ and $-Re(CO)_5$.

It is known that the local symmetry of the $-Rh(CO)_4$ group is C_{3v} and the local symmetry of the $Re(CO)_5$ group is C_{4v}.[27] Figure 3 presents the IR spectra of $BrRe(CO)_5$ and $HRh(CO)_4$[16b,28] obtained in our lab for comparison with the new species. As shown in Figure 3, $BrRe(CO)_5$ has three vibrations at 1986(s), 2016.4(w), and 2046(vs) cm^{-1} and $HRh(CO)_4$ has three metal−carbonyl vibrations at 2041.6(vs), 2071.8(m), and 2123.6(w) cm^{-1}. Assuming that the two " local symmetries"[29] rule holds for a species $(CO)_4Rh-Re(CO)_5$, we would expect six bands, three ($2A_1+1E$) for the $Rh(CO)_4$ part of the molecule and another three ($2A_1+1E$) for the $Re(CO)_5$ part of the molecule. Accordingly, two very strong bands (E) should be found in the spectrum. The intensity ratio of the two very strong bands (E) should be ca.

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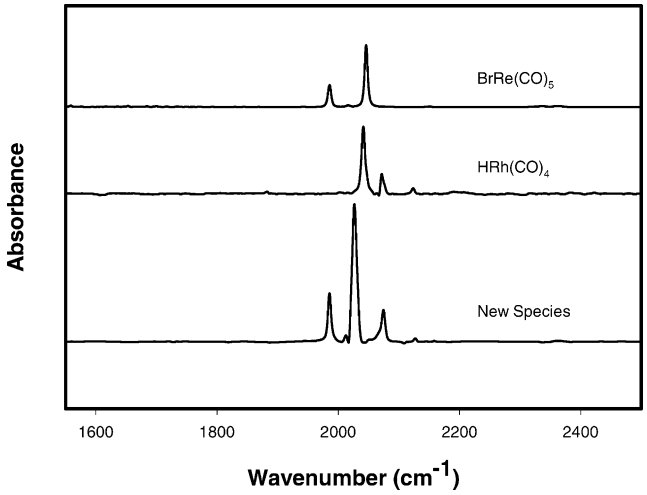
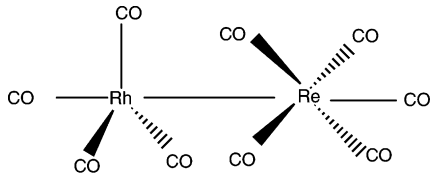


Figure 3. Spectral comparison of the new species with the spectra of $BrRe(CO)_5$ and $HRh(CO)_4$ obtained in our lab.

Scheme 1. Proposed Structure of $RhRe(CO)_9$



3/4, and they should represent ca. 7/9 of the total CO stretching intensities.

Indeed, the new spectrum appears to meet the above assumptions. The two bands 2075(s) and 2127.2(w) cm^{-1} are quite close to the $2A_1$ belonging to the $Rh(CO)_4$ moiety, while the other two bands 1985.6(s) and 2012.2(w) cm^{-1} are quite close to $2A_1$ belonging to the $Re(CO)_5$ moiety. Furthermore, close inspection of the spectrum indicates that the peak at 2026.6 cm^{-1} is very strong and broad (the half-width is ca. 10 cm^{-1} instead of the usual 5 cm^{-1} anticipated) and is accordingly a combination of the two required strong bands (E). Integrated intensities at this position account for ca. 74% of the total CO stretching intensities.

As mentioned in regard to Table 1, the cobalt−rhenium nonacarbonyl is known. Bor et al.[5] reported that $ReCo(CO)_9$ has six peaks at 1971.7(w, br), 1990(s), 2007(w), 2032.8(vs), 2059.8(s), and 2133.9(w) cm^{-1}. Except for the weak broad peak at 1971.7 cm^{-1}, all the other peaks are quite similar to the present new complex. In their assignment, a "free rotational model" was employed to explain the peak at 1971.7 cm^{-1}. Bor et al. also reported that the presence of the isotopic satellite (1956 cm^{-1}) from natural ^{13}C. An ^{13}C isotopic satellite for the lowest vibration at 1944.8 cm^{-1} can be found in the new complex $RhRe(CO)_9$. The proposed structure for $RhRe(CO)_9$ is shown in Scheme 1. The attempts to isolate $RhRe(CO)_9$ by crystallization were unsuccessful. (See Experimental Section for more details.)

Concentration Profiles. Figure 4 shows the time-dependent moles of $Rh_4(CO)_{12}$, $HRe(CO)_5$, and $RhRe(CO)_9$ respectively for experiment 6 (Table 2). As all the peaks of the $HRe(CO)_5$ are overlapping with other species, its calculation is somewhat sensitive.

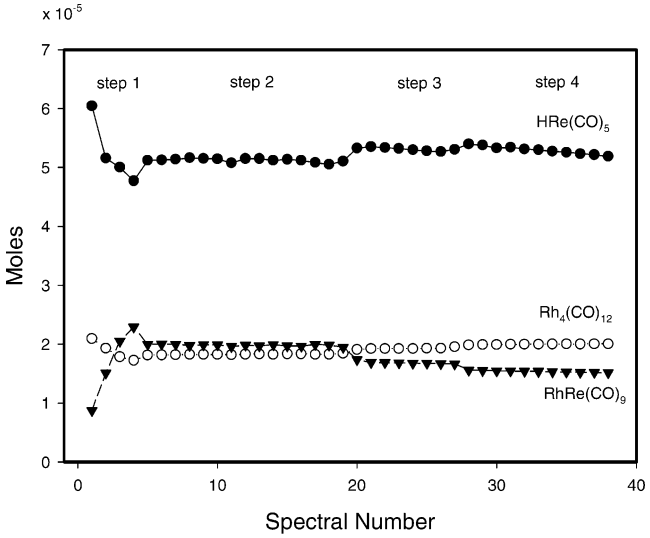


Figure 4. Representative example of the concentration profiles of the organometallic species. This experiment was performed with 250 mL of *n*-hexane at 308.2 K with 0−2.2 MPa CO and 0−2.0 MPa H_2. The initial conditions were 124.9 mg of $Rh_4(CO)_{12}$ and 64.5 μL of $HRe(CO)_5$.

As shown in Figure 4, step 1, with only $Rh_4(CO)_{12}$/$HRe(CO)_5$/CO in the system, the moles of both $Rh_4(CO)_{12}$ and $HRe(CO)_5$ have a very rapid decline, while the moles of $RhRe(CO)_9$ increased rapidly. This means that with little or no molecular hydrogen in the system, the reaction $Rh_4(CO)_{12} + 4HRe(CO)_5 + 4CO \leftrightarrow 4RhRe(CO)_9 + 2H_2$ goes very fast to the right-hand side. In step 2, when molecular hydrogen was added, it can be seen that the $RhRe(CO)_9$ moles decreased, and accordingly the moles of both $Rh_4(CO)_{12}$ and $HRe(CO)_5$ increased until they reached a new equilibrium state. This is clear evidence for the rapid and reversible molecular hydrogen activation by the heterometallic dinuclear carbonyl $RhRe(CO)_9$. In the following steps, with more hydrogen introduced in the reactor, similar trends can be observed in Figure 4.

Thermodynamics. Six series of experiments were conducted at three temperatures to determine the equilibrium constants for the reaction.

$$Rh_4(CO)_{12} + 4HRe(CO)_5 + 4CO \leftrightarrow 4RhRe(CO)_9 + 2H_2 \quad (2)$$

$$K_{eq} = [RhRe(CO)_9]^4[H_2]^2/[Rh_4(CO)_{12}][HRe(CO)_5]^4[CO]^4 \quad (3)$$

In the above equations, all the concentrations were measured in mole fractions. As shown in Table 2, the equilibrium experiments were performed under different partial pressures of CO and H_2 with different initial loadings of $Rh_4(CO)_{12}$ and $HRe(CO)_5$.

The regression analyses yield the equilibrium constants at different temperatures. The equilibrium constants were K_{eq}(289.7 K) = 94 113 (R^2 = 0.88), K_{eq}(298.3 K) = 16 715 (R^2 = 0.99), and K_{eq}(308.2 K) = 3278 (R^2 = 0.89). The R^2 values indicate that two of the three regressions could be better. The difficulties responsible for the two low R^2 values include (1) the known difficulties in measuring the equilibria of very reactive organometallics,[13] i.e., $CoRh(CO)_7$, (2) the deviation in

the CO and H_2 Henry constants in the binary gas vapor−liquid equilibria, and (3) the extremely large values of the exponents in both the numerator and denominator of the equilibrium constant. The latter sixth- and ninth-order dependencies are most surely a significant source of error. Nevertheless, the equilibrium data are consistent with the overall reaction stoichiometry.

The equilibrium thermodynamics was regressed to provide the thermodynamic parameters $\Delta_r H = -116 \pm 29$ kJ/mol and $\Delta_r S = -312 \pm 99$ J/(mol K). The negative value of the enthalpy $\Delta_r H$ is consistent with the observation of higher conversion to the hetero-bimetallic dinuclear complex $RhRe(CO)_9$ at lower temperatures. In addition, the negative sign of the entropy of the reaction $\Delta_r S$ is in agreement with the stoichiometric equation for this reaction; namely, nine molecule reagents give only six molecules as products. Due to the very low experimental ΔP_T used in this study, a three-parameter thermodynamic expression involving $\Delta_r V$ was not used to analyze the data.

Discussion

It was somewhat surprising not to find $Re_2(CO)_{10}$ in the reaction of $HRe(CO)_5/Rh_4(CO)_{12}$ under CO/H_2. Indeed, the $HRe(CO)_5$ might be expected to undergo bimolecular elimination to form $Re_2(CO)_{10}$, but this reaction is apparently negligible under the present conditions.

The formation of $RhRe(CO)_9$ was also attempted without the use of $HRe(CO)_5$. One semibatch experiment was performed with a reactant combination comprising $Re_2(CO)_{10}$ and $Rh_4(CO)_{12}$ in *n*-hexane under 2.0−3.0 MPa CO and 2.0 MPa H_2, at 298−308 K. Spectral analysis with both BTEM and target factor analysis (TFA)[24e] did not provide any evidence for the presence of $ReRh(CO)_9$.

The intrinsic reaction kinetics for the formation of $RhRe(CO)_9$ and/or the activation of molecular hydrogen on $RhRe(CO)_9$ were too rapid to be captured with the present experimental setup. Indeed, characteristic times for gas−liquid mass transfer as well as liquid-phase mixing were on the order of a few minutes.[30] Therefore, it is quite possible, indeed probable, that transport-controlled rather than intrinsic kinetics was observed. Nevertheless, it appears likely that an intermediate such as an unobservable $H_2RhRe(CO)_8$ and/or $H_2RhRe(CO)_7$ is formed and subsequently undergoes fragmentation to give $HRe(CO)_5$ and a very unstable hydridorhodium species such as $HRh(CO)_4$[24b,28] and/or $HRh(CO)_3$,[31] rapidly yielding $Rh_4(CO)_{12}$.

The relatively infrequent identification of a new unsubstituted hetero-bimetallic dinuclear carbonyl probably justifies a small discussion of potential reactivity patterns. Foremost among these reactivity patterns would be the chemistry of the carbonyl ligands. The rapid hydrogen activation on the coordinately saturated $RhRe(CO)_9$ is a certain indication of facile CO dissociation. In this regard, the rapid dissociation of CO and subsequent hydrogen activation is similar to the case of $CoRh(CO)_8$: both occur at room temperature under significant partial pressures of CO. Furthermore, the issue of facile CO dissociation prompts questions about fluxionality. It is well known that the CO ligands on $Rh_4(CO)_{12}$,[32] but more importantly $CoRh(CO)_7/CoRh(CO)_8$, are fluxional on the NMR time scale. This issue is surely one that should be addressed in the future.

The CO dissociation also prompts questions about possible facile substitution reactions. Substitution with 1 equiv of phosphine almost surely occurs, and substitution on the rhodium is the probable position, as is the case for $CoRh(CO)_7 + PEt_3 \rightarrow CoRh(CO)_6PEt_3 + CO$.[33] Analogously, substitutions with NR_3, PPN, etc., can be expected. More complex addition reactions involving unsaturated organic molecules should not be ruled out either. It is known that $CoRh(CO)_7$ readily adds 1 equiv of alkyne ($C_6F_5C{\equiv}CC_6F_5$, $PhC{\equiv}CPh$) to make $CoRh(CO)_6((\mu\text{-}\eta^2\text{-alkyne})$.[34] A related reaction with $RhRe(CO)_9$ may occur.

The known facile CO dissociation and rapid activation of molecular hydrogen and the presumed reactivity toward addition reactions suggest the strong potential for $RhRe(CO)_9$ as a catalyst precursor in a variety of catalytic syntheses, but particularly carbonylations. Future work in this area is planned.

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