Steric Effects in the Oxidative Addition of MeI to a Sulfido-Bridged ZrRh₂ Early-Late Heterobimetallic Compound

Duc Hanh Nguyen, F. Javier Modrego, J. Miguel Cetina-Casas, Daniel Gómez-Bautista, M. Victoria Jiménez, Ricardo Castarlenas, Fernando J. Lahoz, Luis A. Oro^{} and Jesús J. Pérez-Torrente^{*}*

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea-ISQCH,
Universidad de Zaragoza-C.S.I.C., C/ Pedro Cerbuna 12, 50009-Zaragoza, Spain.

AUTHOR EMAIL ADDRESS: perez@unizar.es, oro@unizar.es

Abstract

Reaction of the *early-late* heterobimetallic compound $[\text{Cp}^{\text{t}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(\text{CO})\}_2(\mu\text{-dppm})]$ (**1**) with MeI affords the unusual oxidative addition product $[\text{Cp}^{\text{t}}_2\text{Zr}(\mu_3\text{-S})_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-dppm})(\text{I})(\text{COCH}_3)]$ (**4**) showing the presence of a bridging carbonyl and a terminal acetyl ligand. The optimized structure of **4** by DFT calculations is further substantiated by the spectroscopic data of the ^{13}CO -labeled complex **4***. The same reaction carried out on the structurally related *gem*-dithiolate dinuclear complexes $[\text{Rh}_2(\mu\text{-S}_2\text{CR}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (**2**, **3**) gives the one-center oxidative addition acetyl products $[\text{Rh}_2(\mu\text{-S}_2\text{CR}_2)(\text{COCH}_3)(\text{I})(\text{CO})(\text{PPh}_3)_2]$ ($\text{R}_2 = -(\text{CH}_2)_5-$, **5**; $\text{R} = \text{Bn}$ (benzyl), **6**). Reaction of **3** with molecular iodine affords the dinuclear compounds $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{I})_2(\mu\text{-CO})(\text{PPh}_3)_2]$ (**7**) and $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{I})_2(\text{CO})_2(\text{PPh}_3)_2]$ (**8**), the transannular oxidative addition product, in a 40:60 ratio. Compound **7** was also formed in the reaction of **3** with MeI after a prolonged reaction time. The molecular structures of compounds **5** and **7** have been determined by X-ray analyses. A Natural Bond Orbital (NBO) analysis has shown an analogous bonding scheme in the “ $\text{Rh}_2(\mu\text{-CO})\text{P}_2$ ” subunit of complexes **4** and **7**. Although both complexes can be formally described as composed of a Rh(III)-Rh(III) unit assuming a ketonic character of the bridging carbonyl ligand, the natural charges on the rhodium atoms and the WBI indexes for the Rh-Rh and CO bonds points out to electronically unsaturated metal centers bridged by a carbonyl ligand lacking ketonic character and a significant metal-metal interaction. In addition, DFT calculations on reaction pathway leading to the formation of **4** evidenced the key role of the bulky “ $\text{Cp}^{\text{t}}_2\text{Zr}$ ” fragment in the course of the reaction.

Introduction

The oxidative addition reaction is a fundamental process in organometallic chemistry with significant implication in many important catalytic reactions.¹ In particular, the oxidative addition of methyl iodide followed by methyl migration is the key step in the catalytic carbonylation of methanol to acetic acid.^{2,3} Major research efforts in this particular process have been devoted to improve the catalytic activity and stability of the rhodium catalysts by ligand design, and to study the effects of the ancillary ligands on the rates of oxidative addition and migratory carbonyl insertion steps.^{4,5} In this context, it has been observed that the catalytic activity is determined by a complex interplay between electronic and steric effects introduced by the auxiliary ligands, the latter being of key importance in promoting the carbonyl insertion.⁶

Methyl iodide activation by dinuclear late transition-metal complexes in which a folded bridging framework holds coordinatively unsaturated d^8 sites in close proximity has also received considerable attention.⁷ With the aim of exploring the possible cooperative effects between the metal centers, the oxidative addition of a range of electrophiles on a number of d^8 rhodium and iridium dinuclear complexes having thiolato, pyrazolato, 7-azaindolato, amido or functionalized pyridine ligands have been investigated.⁸ As a general trend, the reactivity of dinuclear iridium(I) complexes is directed to the formation of metal-metal bonded Ir(II)-Ir(II) compounds as a result of the two-center oxidative addition.⁹ In sharp contrast, dinuclear rhodium(I) complexes frequently undergo double one-center oxidative addition to afford Rh(III)-Rh(III) species.¹⁰ The oxidative addition of methyl iodide on dinuclear rhodium carbonyl complexes generally results in the formation of acetyl derivatives. However, in this case, both mixed-valence Rh(III)-Rh(I) acetyl or Rh(III)-Rh(III) diacetyl complexes are the standard outcome of this reaction.¹¹

We have recently described the straightforward synthesis of dinuclear *gem*-dithiolato bridged rhodium complexes $[\text{Rh}_2(\mu\text{-S}_2\text{CR}_2)(\text{cod})_2]$ from the corresponding *gem*-dithiol $\text{R}_2\text{C}(\text{SH})_2$ compounds.

Carbonylation of these diolefin compounds followed by reaction with P-donor ligands allowed the stereoselective preparation of the *trans* isomer of the disubstituted complexes $[\text{Rh}_2(\mu\text{-S}_2\text{CR}_2)(\text{CO})_2(\text{PR}'_3)_2]$ ($\text{R} = \text{Bn}$ (benzyl), $\text{R}_2 = -(\text{CH}_2)_5-$; $\text{R}' = \text{Ph}, \text{Cy}$).^{12,13} Compared to dinuclear rhodium thiolato and dithiolato bridged complexes, the presence of a single bridge-head carbon atom between both sulfur atoms results in a more rigid and compact core with a smaller angle between the coordination planes of the rhodium centers and shorter metal–metal distances, which favour the cooperative effects between the metal centers.¹³ On the other hand, a similar synthetic strategy using the bis-hydrosulfido zirconium complex $[\text{Cp}^{\text{tt}}_2\text{Zr}(\text{SH})_2]$ provide access to unusual *early-late* d^0 - d^8 sulfido-bridged complexes $[\text{Cp}^{\text{tt}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(\text{diolefin})\}_2]$ and $[\text{Cp}^{\text{tt}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(\text{CO})_2\}_2]$ ($\text{Cp}^{\text{tt}} = \eta^5\text{-1,3-di-tert-butylcyclopentadienyl}$).¹⁴ The metallocene fragment “ $\text{Cp}^{\text{tt}}_2\text{Zr}$ ” in these complexes, composed of an electron deficient metal center and bulky substituents, introduce important electronic and steric effects into the dinuclear framework that could result in a unique reactivity. However, the reactivity studies dealing with oxidative additions on *early-late* metal complexes are scarce in spite of their potential for cooperative effects between such significantly different metal centers.¹⁵ In this context, we have reported the reactivity of a sulfido-bridged TiIr_2 carbonyl compound with iodoalkanes giving the two-fragment two-center oxidative addition products with the concomitant formation of an iridium-iridium bond in a stereoselective way.¹⁶

Interestingly, the ZrRh_2 sulfido-bridged clusters and the dinuclear *gem*-dithiolato bridged rhodium complexes are structurally related if they are seen as composed of a rhodium dinuclear subunit bridged by two sulfido ligands. Thus, the *gem*-dithiolato bridged complexes can be considered as the “carbon” equivalents of the trigonal-bipyramidal core $[\text{ZrRh}_2(\mu_3\text{-S})_2]$ in the heterometallic clusters (Scheme 1). We report herein a comparative study of the reactivity of both types of complexes toward the electrophiles methyl iodide and iodine. This study has allowed discovering an unexpected outcome in the oxidative addition of methyl iodide to the *early-late* ZrRh_2 compound that has been rationalized on

the basis of the steric effects imparted by the metallocene fragment.

Scheme 1

Results and discussion

Selection of suitable ZrRh_2 and Rh_2 precursors. In order to study the influence of the *early* metallocene fragment on the outcome of the oxidative additions, the choice of suitable precursors was required. Although the carbonyl complexes $[\text{Cp}^{\text{t}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(\text{CO})_2\}_2]$ and $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{CO})_4]$ are accessible in good yields,^{12,14} previous results in our group suggested to carry out this study on phosphine substituted carbonyl complexes in order to increase the nucleophilic character of the metal centers.

The replacement of carbonyl ligands in $[\text{Cp}^{\text{t}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(\text{CO})_2\}_2]$ by monodentate P-donor ligands is unselective and gives both *cis* and *trans* isomers of the disubstituted complexes $[\text{Cp}^{\text{t}}_2\text{Zr}(\mu_3\text{-S})_2\text{Rh}_2(\text{CO})_2(\text{PR}_3)_2]$. In addition, the steric influence of the bulky phosphine ligands induces restrictions to the rotation of the Cp^{t} rings resulting in the existence of rotamers in both isomers (eclipsed and staggered) which makes them inappropriate for reactivity studies. In contrast, the compound $[\text{Cp}^{\text{t}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(\text{CO})\}_2(\mu\text{-dppm})]$ (**1**) (dppm = diphenylphosphino methane) exists as a single *cisoid* isomer with no restrictions to the rotation of the Cp^{t} rings.¹⁴ Unfortunately, we do not have evidence on the formation of dinuclear complexes of the type $[\text{Rh}_2(\mu\text{-S}_2\text{CR}_2)(\text{CO})_2(\mu\text{-dppm})]$ ($\text{R} = \text{Bn}$; $\text{R}_2 = -(\text{CH}_2)_5-$) in the reaction of *gem*-dithiolato carbonyl complexes with dppm. However, the complexes $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**) ($\text{Chxn} = 1,1\text{-cyclohexylene}$)¹³ and $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (**3**)¹² (*trans* isomers, 97%), having cyclohexanedithiolato and 1,3-diphenyl-2,2-dithiolatopropane ligands,

respectively, have been obtained in high yield. Thus, in view of the problems associated with preparation of structurally related complexes having identical auxiliary ligands, we decided to study the reactivity of complexes **1-3** toward the electrophiles methyl iodide and iodine.

Reaction of $[\text{Cp}^{\text{t}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(\text{CO})\}_2(\mu\text{-dppm})]$ (1**) with MeI.** A dark green solution of compound $[\text{Cp}^{\text{t}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(\text{CO})\}_2(\mu\text{-dppm})]$ (**1**) in neat MeI quickly turned brown-red in a few minutes due to the formation of the heterobimetallic compound $[\text{Cp}^{\text{t}}_2\text{Zr}(\mu_3\text{-S})_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-dppm})(\text{I})(\text{COCH}_3)]$ (**4**) (Scheme 2). Compound **4** was isolated as a microcrystalline dark brown-red solid in excellent yield and has been fully characterized by elemental analysis, FAB-MS spectrum, IR and multinuclear NMR spectroscopy.

Scheme 2. Oxidative addition of MeI to the ZrRh₂ compound **1**.

The nuclearity of **4** as a ZrRh₂ compound was established by the FAB⁺ spectrum in CH₂Cl₂ that showed several peaks corresponding to the loss of carbonyl, methyl and iodido ligands. Compound **4** is no conductor in acetone. The IR of **4** in CH₂Cl₂ showed no absorptions in the terminal carbonyl-stretching region although a broad $\nu(\text{CO})$ band was observed at 1788 cm⁻¹ that might correspond to the stretching mode of bridging carbonyl or acetyl ligands. The ¹H NMR of **4** in CDCl₃ evidenced inequivalent Cp^t ligands and consequently, six triplets ($J_{\text{P-H}} \approx 2.6$ Hz) between δ 6.50 and 5.83 ppm and four singlets between δ 1.38 and 1.05 ppm were observed for the protons of the cyclopentadienyl rings and ^tBu groups, respectively. In addition, the spectrum also showed a singlet at δ 2.44 ppm that was assigned to the methyl resonance of an acetyl ligand. The ³¹P{¹H} NMR in CDCl₃ displays a symmetric

complex resonance centered at δ 28.3 ppm (Figure 1a) that correspond to an ABXY spin system (A, B = ^{31}P and X, Y = ^{103}Rh). The observed signal correlates well with the calculated spectra using the following parameters: $\delta_{\text{A}} = 29.10$ ppm, $\delta_{\text{B}} = 27.49$ ppm, $J_{\text{Rh-P}} = 168.59$ Hz and $^2J_{\text{P-P}} = 38.95$ Hz (Figure 1b). Both inequivalent P-donor atoms of the dppm ligand are coupled to different rhodium atoms with identical $J_{\text{Rh-P}}$ coupling constant and between them with a relatively small $P_{\text{A}}\text{-}P_{\text{B}}$ coupling. Unfortunately, **4** is unstable in dichloromethane or benzene solutions after a prolonged period of time, which prevented registering its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum or growing a single crystal to determine the molecular structure.

Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** at 298 K in CDCl_3 : experimental (a) and simulated (b)

In order to get structural information on **4** we have prepared the ^{13}CO -labeled $[\text{Cp}^{\text{tt}}_2\text{Zr}(\mu_3\text{-S})_2\text{Rh}_2(\mu\text{-}^{13}\text{CO})(\mu\text{-dppm})(\text{I})(^{13}\text{COCH}_3)]$ (**4***) complex. The carbonylation (^{13}CO) of a mixture of $[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2$ and benzyltriphenylphosphonium chloride in dichloromethane/methanol gave a pale yellow solution of the anion $[\text{RhCl}_2(^{13}\text{CO})_2]^-$ in less than half hour.¹⁷ Further reaction with $[\text{Cp}^{\text{tt}}_2\text{Zr}(\text{SH})_2]$ and NEt_3 afforded

$[\text{Cp}^{\text{tt}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(^{13}\text{CO})_2\}_2]$ which was isolated as an emerald-green solid in 78% yield. The reaction of this compound with dppm in CDCl_3 gave $[\text{Cp}^{\text{tt}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(^{13}\text{CO})\}_2(\mu\text{-dppm})]$ (**1***) that was further reacted with MeI at 50 °C to give a solution of complex **4***.

Figure 2. Carbonyl region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4*** in CDCl_3 at 298 K.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4*** in the carbonyl region displays two strongly coupled resonances at δ 232.09 ppm and 217.81 ppm that correspond to an acetyl and a bridging carbonyl ligands, respectively (Figure 2). The resonance of the acetyl ligand is seen as a dd by coupling to rhodium ($^1J_{\text{Rh-C}} = 11.05$ Hz) and phosphorus ($^2J_{\text{P-C}} = 5.0$ Hz) whereas the resonance of the bridging carbonyl ligand is a ddt by coupling both to the two rhodium atoms ($^1J_{\text{Rh-C}} = 40.60$ Hz and $^1J_{\text{Rh-C}} = 49.35$ Hz) and the two phosphorus atoms of the bridging dppm ligand with the same coupling constant ($^2J_{\text{P-C}} = 8.69$ Hz). As expected, the methyl resonance of the acetyl ligand, $^{13}\text{COCH}_3$, was observed as a doublet at δ 2.42 ppm in the ^1H NMR spectrum with a $^2J_{\text{C-H}}$ of 5.7 Hz. The chemical shift for the acetyl carbon is in the expected region for a terminal acetyl ligand and rules out the presence of a bridging acetyl group.¹⁸ The $^{31}\text{P}\{^1\text{H}\}$ NMR of **4*** in CDCl_3 showed a unsymmetric complex resonance centered at δ 28.3 ppm (Figure 3a) that has been successfully simulated as the AB part of the ABMNXY spin system (A, B = ^{31}P ; M, N = ^{13}C ; X, Y = ^{103}Rh) using the parameters obtained from the $^{31}\text{P}\{^1\text{H}\}$ NMR of **4** (Figure 3b). The shape of this resonance is a consequence of the different coupling scheme for both P-donor atoms of the bridging dppm ligand. Thus, the strong-coupled left part of the signal corresponds to the P atom bonded

to the rhodium atom coordinated to the acetyl ligand (δ 29.10 ppm) that is coupled to both $^{13}\text{COCH}_3$ and bridging ^{13}CO ligands. The right part of the signal corresponds to the other P atom that is only under the influence of the bridging ^{13}CO ligand (δ 27.49 ppm).

Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4*** at 298 K in CDCl_3 : experimental (a) and simulated (b).

The DFT geometry-optimized structure of $[\text{Cp}^{\text{H}}_2\text{Zr}(\mu_3\text{-S})_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-dppm})(\text{I})(\text{COCH}_3)]$ (**4**) is shown in Figure 4. The calculated Rh-Rh distance is 2.809 Å, slightly shorter than the calculated for the parent compound **1**, 2.817 Å (experimental 2.741 Å).^{14a} A Natural Bond Orbital (NBO) analysis¹⁹ shows some relevant features regarding the metal-metal interaction and the role of the bridging carbonyl ligand in **4** (Table 1). Although the calculated metal-metal distance for **4** is very similar to that of the Rh(I)-Rh(I) in **1**, the calculated Wiberg bond index (WBI) (0.145) points to the existence of a metal-metal bond in the former and its absence in the starting Rh(I) compound, where the WBI between the rhodium atoms is just 0.050. The value for **4** is close to the value of 0.13 found by us for the Rh-Rh bond in the related *early-late* heterobimetallic compound $[\text{Cp}^{\text{H}}_2\text{Zr}(\mu_3\text{-S})_2\text{Rh}(\mu\text{-CO})_2(\mu\text{-dppm})\text{Rh}(\text{I})(\eta^2\text{-dppm})]$ ²⁰ and

is similar to the reported for second row transition metal compounds having single metal-metal bonds bridged by carbonyl ligands.^{21, 22} The oxidation of the rhodium centers is reflected in the increase of positive charge which goes from a mean of -0.089 in the Rh(I)-Rh(I) compound **1** to +0.204 in the calculated structure of **4**. In order to analyze the effect of the bridging carbonyl ligands on the WBI of metal-metal bonds we have calculated the structure of the hypothetical isomer $[\text{Cp}^{\text{u}}_2\text{Zr}(\mu_3\text{-S})_2\text{Rh}_2(\text{CO})(\mu\text{-dppm})(\text{I})(\text{COCH}_3)]$, unbridged by the CO ligand. This isomer shows a significantly shorter Rh-Rh distance (2.568 Å) and a larger WBI (0.373), which is in agreement with the observed effect of bridging carbonyl ligands lowering the WBI of metal-metal bonds.²¹ The bridging carbonyl ligand in **4** shows a WBI of 1.907 and a net charge of -0.045 for the whole ligand. The comparison of these values with both, the terminal carbonyl ligand of the hypothetical isomer and the carbonyl of the acetyl ligand in both the bridged and unbridged isomers, is illustrative. The carbonyl bridge has a net NBO charge of -0.045 whereas moving to a terminal position leads to a high net charge +0.180 and the WBI goes from 1.907 to 2.183 respectively, which shows a poorer π -acceptor role. On the other side the carbonyl group on the acetyl ligand has a mean charge (for both isomers) of -0.1 and a mean WBI of 1.76, which reflects the lower formal order of two expected for an acetyl carbonyl group. These data indicate that in spite of the increase of the electron density on the carbonyl ligand and the relaxation of the bond strength, which is also reflected in the IR spectrum, the bridging carbonyl ligand in **4** is still far from playing a net ketonic role (CO^{2-}). Thus, the bonding scheme in the dirhodium subunit of **4** is best described as intermediate between these two extreme bonding situations: i) a Rh(III)-Rh(III) unit having a ketonic carbonyl bridging ligand with no significant metal-metal interaction, and ii) a metal-metal bonded Rh(II)-Rh(II) unit with a bridging carbonyl ligand.

Rh...Rh	2.809 Å
Rh-C _μ	1.957 Å
Rh-C _μ	1.982 Å
C-O	1.184 Å
Rh-C _μ	90.98°

Figure 4. DFT geometry-optimized structure of $[\text{Cp}_2^{\text{t}}\text{Zr}(\mu_3\text{-S})_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-dppm})(\text{I})(\text{COCH}_3)]$ (**4**).

Table 1. Relevant natural charges and Wiberg bond indexes (WBI) obtained by NBO analysis in *early-late* ZrRh_2 heterobimetallic complexes.

Compound	Natural charges	WBI
<p>1</p>	Rh ¹ (-0.097)	Rh ¹ Rh ² (0.050)
	Rh ² (-0.081)	CO ¹ (2.064)
	C ¹ (0.542)	CO ² (2.072)
	O ¹ (-0.482)	
	C ² (0.547)	
	O ² (-0.480)	
<p>4</p>	Rh ¹ (0.206)	Rh ¹ Rh ² (0.145)
	Rh ² (0.201)	CO ^a (1.742)
	C ^a (0.485)	CO ^μ (1.907)
	O ^a (-0.585)	
	C ^μ (0.463)	
	O ^μ (-0.508)	
<p>5</p>	Rh ¹ (0.115)	Rh ¹ Rh ² (0.373)
	Rh ² (0.155)	CO ^a (1.783)
	C ^a (0.480)	CO ^t (2.183)
	O ^a (-0.571)	
	C ^t (0.606)	
	O ^t (-0.420)	

Reaction of $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PPh}_3)_2]$ (2**) and $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (**3**) with MeI.**

The dissolution of compound **2** in neat MeI gave a dark red solution of the acetyl derivative $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{COCH}_3)(\text{I})(\text{CO})(\text{PPh}_3)_2]$ (**5**) in one hour (Scheme 3). The compound was obtained as a brown-red microcrystalline solid in 87% yield after recrystallization of the crude compound in benzene/diethyl ether.

Compound **5** results from the one-center MeI oxidative addition followed by methyl migration leading to a mixed-valence Rh(III)-Rh(I) acetyl species. The IR spectrum of **5** in dichloromethane showed two strong broad $\nu(\text{CO})$ bands at 1985 and 1683 cm^{-1} that correspond to the terminal carbonyl and acetyl ligands, respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR in CD_2Cl_2 features two doublet of doublets for the inequivalent PPh_3 ligands at δ 38.41 and 37.62 ppm with coupling constants of $J_{\text{Rh-P}} = 158.1$ Hz and 146.0 Hz, respectively, and a $J_{\text{P-P}}$ of 5.0 Hz. The low field region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CD_2Cl_2 features two resonances at δ 216.9 (dd) and 188.3 (dd) ppm corresponding to the $\text{CH}_3\text{CO-}$ and terminal carbonyl ligands, respectively. In addition, the methyl group of the acetyl ligand was observed in the ^1H NMR spectrum as a singlet at δ 3.30 ppm.

Scheme 3. Oxidative addition of MeI to *gem*-dithiolato-bridged dinuclear rhodium complexes.

The molecular structure of **5** determined by a single crystal analysis is shown in Figure 5 and a

selection of bond distances and angles are collected in Table 2. The dinuclear skeleton of **5** is held up by a 1,1-cyclohexanedithiolato ligand exhibiting a $1:2\kappa^2S, 1:2\kappa^2S'$ coordination mode. The coordination geometry of the Rh(1) atom, formally a Rh(III) center, is distorted square-pyramidal with the acetyl ligand at the apical position and the terminal iodido and a triphenylphosphino ligands at basal sites. The Rh(2) atom, formally a Rh(I) center, exhibit a distorted square-planar coordination. The main source of distortion arises from the geometrical constraints imposed by the *gem*-dithiolato ligand with S(1)-Rh(1)-S(2) and S(1)-Rh(2)-S(2) bond angles of 70.24 and $69.76(3)^\circ$, respectively; slightly smaller than in the parent complex $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**) (average $71.07(2)^\circ$).¹³ These angles are influenced by the narrow S(1)-C(4)-S(2) angle of $94.89(16)^\circ$ centered on the bridgehead carbon atom of the 1,1-cyclohexanedithiolato ligand ($96.82(12)^\circ$ in **2**). The PPh_3 ligands coordinated to both rhodium atoms adopt a mutually *trans* disposition as in complex **2**. On the other hand, the Rh...Rh distance of $2.9053(4)$ Å is very similar to that found in complex **2** ($2.8903(3)$ Å) and slightly longer than the found in related *gem*-dithiolato rhodium(I) dimers having 1,5-cyclooctadiene as auxiliary ligands $[\text{Rh}_2(\mu\text{-S}_2\text{CR}_2)(\text{cod})]$ ($\text{R} = \text{Bn}, i\text{Pr}$; $\text{R}_2 = -(\text{CH}_2)_4-$; $2.8544(5)$ - $2.8674(3)$ Å).¹²

Figure 5. Molecular structure of $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{COCH}_3)(\text{I})(\text{CO})(\text{PPh}_3)_2]$ (**5**).

Table 2. Selected bond distances (Å) and angles (°) for the dinuclear complex [Rh₂(μ-S₂Chxn)(COCH₃)(I)(CO)(PPh₃)₂] (**5**).

Rh(1)-I	2.6860(4)	Rh(1)··Rh(2)	2.9053(4)
Rh(1)-P(1)	2.3041(9)	Rh(2)-P(2)	2.2906(10)
Rh(1)-S(1)	2.3301(9)	Rh(2)-S(1)	2.3864(9)
Rh(1)-S(2)	2.4398(9)	Rh(2)-S(2)	2.4146(9)
Rh(1)-C(1)	1.979(4)	Rh(2)-C(3)	1.837(4)
C(1)-O(1)	1.205(5)	C(3)-O(3)	1.149(5)
C(1)-C(2)	1.518(5)		
Rh(2)-Rh(1)-I	111.36(1)		
Rh(2)-Rh(1)-P(1)	106.92(3)	Rh(1)-Rh(2)-P(2)	126.00(3)
Rh(2)-Rh(1)-S(1)	52.86(2)	Rh(1)-Rh(2)-S(1)	51.11(2)
Rh(2)-Rh(1)-S(2)	52.84(2)	Rh(1)-Rh(2)-S(2)	53.64(2)
Rh(2)-Rh(1)-C(1)	146.81(11)	Rh(1)-Rh(2)-C(3)	114.62(12)
P(1)-Rh(1)-S(1)	94.80(3)	P(2)-Rh(2)-S(1)	172.30(3)
P(1)-Rh(1)-S(2)	159.37(3)	P(2)-Rh(2)-S(2)	102.70(3)
P(1)-Rh(1)-C(1)	90.54(11)	P(2)-Rh(2)-C(3)	92.13(12)
S(1)-Rh(1)-S(2)	70.24(3)	S(1)-Rh(2)-S(2)	69.76(3)
S(1)-Rh(1)-C(1)	98.70(11)	S(1)-Rh(2)-C(3)	95.49(12)
S(2)-Rh(1)-C(1)	105.39(11)	S(2)-Rh(2)-C(3)	164.85(12)
I-Rh(1)-P(1)	95.80(2)	Rh(2)-C(3)-O(3)	175.4(3)
I-Rh(1)-S(1)	163.24(3)	Rh(1)-C(1)-O(1)	123.3(3)
I-Rh(1)-S(2)	96.03(2)	Rh(1)-C(1)-C(2)	115.7(3)
I-Rh(1)-C(1)	94.14(11)	O(1)-C(1)-C(2)	121.0(3)
Rh(1)-S(1)-Rh(2)	76.03(3)	Rh(1)-S(2)-Rh(2)	73.52(3)
Rh(1)-S(1)-C(4)	91.72(12)	Rh(1)-S(2)-C(4)	88.50(12)
Rh(2)-S(1)-C(4)	83.97(12)	Rh(2)-S(2)-C(4)	83.30(12)

In the same way, the dinuclear compound **3** reacted with neat MeI to give the compound $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{COCH}_3)(\text{I})(\text{CO})(\text{PPh}_3)_2]$ (**6**) which was isolated as a brown-red microcrystalline solid in 84% yield after recrystallization from dichloromethane/diethyl ether. The spectroscopic data for **6** are very similar to those described for **5** and consequently should be isostructural (Scheme 3). In particular, the $^{31}\text{P}\{^1\text{H}\}$ NMR in C_6D_6 (400 MHz) showed a triplet-like resonance that results from the overlap of two doublet of doublets due to the very close chemical shifts, δ 38.30 and 37.45 ppm, and similar $J_{\text{Rh-P}}$ coupling constants of 145.6 and 156.7 Hz ($J_{\text{P-P}} = 4.9$ Hz). The lack of symmetry in the molecule became evident in the ^1H NMR spectrum in CD_2Cl_2 that showed four doublet resonances between δ 4.35 and 3.05 ppm ($J_{\text{H-H}} = 14.9$ and 14.6 Hz) for the inequivalent benzylic protons of the *gem*-dithiolato bridging ligand. The acetyl ligand in **6** was observed as a singlet at δ 3.29 ppm in the ^1H NMR spectrum and as a ddd at δ 218.3 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2), due to the coupling to rhodium ($J_{\text{Rh-C}} = 25.3$ Hz) and to both inequivalent phosphorous atoms ($J_{\text{P-C}} = 5.5$ and 0.3 Hz). In contrast, the terminal carbonyl ligand at δ 187.8 ppm features a dd with standard $J_{\text{Rh-C}}$ and $J_{\text{P-C}}$ coupling constants of 76.8 and 17.2 Hz. As expected, the IR spectrum of **6** showed two $\nu(\text{CO})$ bands at 1988 and 1682 (s) cm^{-1} .

It is worth mentioning that the outcome of the IMe oxidative addition on carbonyl rhodium(I) *gem*-dithiolato complexes is similar to that observed in related dinuclear complexes having simple thiolato bridging ligands, $[\text{Rh}(\mu\text{-SR})(\text{CO})(\text{PR}_3)]_2$, where the PR_3 ligands are usually in a *cis* arrangement to accommodate the *anti* conformation of the thiolato ligands.²³ These results indicate that the geometrical constraints imposed by the *gem*-dithiolato ligands do not influence the chemical reactivity. Thus, reaction of $[\text{Rh}(\mu\text{-S}^t\text{Bu})(\text{CO})(\text{PMe}_2\text{Ph})]_2$ with MeI also gives the mixed-valence Rh(III)-Rh(I) species $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{COCH}_3)(\text{I})(\text{CO})(\text{PMe}_2\text{Ph})_2]$.²⁴ However, this compound exhibits larger S-Rh-S angles of 80.5(1) and 80.3(1)°, a longer Rh...Rh distance of 3.110(1) Å, and a smaller Rh-Rh-C angle involving the acetyl ligand 141.3(1)° than in **5** (Rh(2)-Rh(1)-C(1) 146.81(11)°).

The intermetallic distance found in complex **5**, very similar to the found in the starting material **2**, is

not indicative of the presence a metal-metal bond between both coordinatively unsaturated rhodium centers. However, the spectroscopic data in complexes **5** and **6** suggest the presence of a dative bonding interaction Rh(I)→Rh(III) between the metal centers.²⁵ A first indication of that interaction is the similar chemical shifts and $J_{\text{Rh-P}}$ coupling constants observed for the inequivalent PPh₃ ligands bonded to the electronically very different Rh(I) and Rh(III) metal atoms. In addition, the terminal carbonyl stretching $\nu(\text{CO})$ that was observed at 1960 and 1967 cm⁻¹ in the precursor complexes **2** and **3**, respectively, is shifted to higher wave numbers in complexes **5** and **6**, $\Delta\nu$ of 25 and 21 cm⁻¹. However, the Rh-P bond distances observed in **5** for both metals showed quite similar values, 2.3041(9) for Rh(1) and 2.2906(10) for Rh(2).

In order to determine the extent of the potential metal-metal interaction in this type of complexes, the structure of the pairs **2** and **5**, and, **3** and **6**, have been calculated by DFT. Compounds **2** and **3** show very similar geometries, with rhodium atoms in a square planar environment and separated by a distance of 3.091 Å and 3.040 Å, respectively. The Natural Population Analysis (NPA) charges confirm the asymmetry of the charge distribution in the acetyl derivatives **5** and **6** and support their formulation as formally Rh(III)-Rh(I) mixed valence compounds (Table 3). The NPA charges on the Rh(I) atoms of **5** and **6**, -0.161 and -0.142, are similar to that found on the parent Rh(I) compounds, whereas the charge on the acetyl-bonded Rh(III) atoms increases sensibly to 0.136 and 0.143, respectively. The slight and identical increase of the charge in the Rh(I) center in **5** and **6** (+0.02) is probably due to an inductive effect of the opposite Rh(III) center through the bridging ligands. On the other hand, the Rh-Rh WBI values in **5** and **6**, 0.061 and 0.060, are only slightly higher than the calculated in the starting Rh(I) parent compounds, 0.036 and 0.039, respectively. The calculated WBI values are far from that found in other metal-metal bonded species presented in this paper, which suggests that there is not a significant direct metal-metal interaction in both complexes. Thus, in accordance with the theoretical calculations complexes **5** and **6** are best described as composed of two not directly interacting unsaturated 16 e⁻ Rh(I)

and Rh(III) centers.

Table 3. Relevant natural charges and Wiberg bond indexes (WBI) obtained by NBO analysis in *gem*-dithiolato-bridged dinuclear rhodium complexes.

Compound	Natural charges	WBI
<p style="text-align: center;">2</p>	Rh ¹ (-0.177)	Rh ¹ Rh ² (0.036)
	Rh ² (-0.181)	C ¹ O ¹ (2.071)
	C ¹ (0.558)	C ² O ² (2.069)
	O ¹ (-0.485)	
	C ² (0.555)	
	O ² (-0.486)
<p style="text-align: center;">3</p>	Rh ¹ (-0.162)	Rh ¹ Rh ² (0.039)
	Rh ² (-0.161)	C ¹ O ¹ (2.074)
	C ¹ (0.550)	C ² O ² (2.065)
	O ¹ (-0.481)	
	C ² (0.528)	
	O ² (-0.483)
<p style="text-align: center;">5</p>	Rh ¹ (0.136)	Rh ¹ Rh ² (0.061)
	Rh ² (-0.161)	C ^a O ^a (1.812)
	C ^a (0.545)	C ^t O ^t (2.088)
	O ^a (-0.545)	
	C ^t (0.551)	
	O ^t (-0.471)
<p style="text-align: center;">6</p>	Rh ¹ (0.143)	Rh ¹ Rh ² (0.060)
	Rh ² (-0.142)	C ^a O ^a (1.858)
	C ^a (0.526)	C ^t O ^t (2.088)
	O ^a (-0.504)	
	C ^t (0.550)	
	O ^t (-0.473)	

In an attempt to grow crystals of **6** from the crude compound obtained after longer reaction times we got

a crop of golden yellow microcrystals of the new compound $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{I})_2(\mu\text{-CO})(\text{PPh}_3)_2]$ (**7**).

Figure 6. Molecular structure of $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{I})_2(\mu\text{-CO})(\text{PPh}_3)_2]$ (**7**).

The molecular structure of compound **7** is shown in Figure 6 and selected bond distances and angles are collected in Table 4. The structure consists of a folded Rh_2S_2 core with an additional bridging carbonyl ligand. In the solid state, this molecule exhibits a crystallographic imposed C_2 symmetry with the two-fold axis passing through the bridging carbonyl and the bridgehead carbon C(2) of the *gem*-dithiolate ligand. Both rhodium centers display a distorted square-pyramidal geometry by coordination to both sulfur atoms of the bridging dithiolato ligand, two terminal triphenylphosphine and iodido ligands, and showing the bridging carbonyl ligand in the apical position. The imposed symmetry generates a pseudo-*trans* disposition of ligands at both rhodium atoms. The small S-C(2)-S' angle of $96.4(4)^\circ$ centered on the bridgehead carbon atom of the 1,3-diphenyl-2,2-dithiolato-propane ligand determines a compact core with a reduced S-Rh-S' angle of $71.03(6)^\circ$ and a short Rh...Rh distance, $2.8230(9)$ Å. This complex can be formally described as a Rh(III)-Rh(III) dimer assuming a ketonic

character of the bridging carbonyl ligand with a sp^2 hybridization for the carbon atom.²⁶ In fact, the low $\nu(\text{CO})$ absorption frequency at 1675 cm^{-1} is in the range expected for organic carbonyls and typical of ketonic carbonyl ligands. However, the structural parameters of the bridging CO ligand, C(1)-O $1.156(9)\text{ \AA}$ and Rh-C(1)-O $134.36(16)^\circ$, do not agree well with this ketonic character. On the other hand, the short metal-metal distance results in a small Rh-C(1)-Rh' angle of $91.3(3)^\circ$, in the range of the observed values for carbonyl ligands bridging metal-metal bonded centers.²⁷

Table 4. Selected bond distances ($\text{\AA}$) and angles ($^\circ$) for complex $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{I})_2(\mu\text{-CO})(\text{PPh}_3)_2]$ (**7**).

$\text{Rh}\cdots\text{Rh'}$	2.8230(9)	Rh-S'	2.4068(14)
Rh-I	2.6420(6)	Rh-C(1)	1.974(5)
Rh-P	2.2830(15)	C(1)-O	1.156(9)
Rh-S	2.3718(14)		
$\text{Rh'}\cdots\text{Rh-I}$	124.78(2)	I-Rh-P	94.52(4)
$\text{Rh'}\cdots\text{Rh-P}$	127.46(4)	I-Rh-S	162.21(4)
$\text{Rh'}\cdots\text{Rh-S}$	54.36(4)	I-Rh-S'	94.31(4)
$\text{Rh'}\cdots\text{Rh-S'}$	53.22(4)	I-Rh-C(1)	101.02(10)
$\text{Rh'}\cdots\text{Rh-C(1)}$	44.36(16)	S'-Rh-C(1)	87.74(14)
P-Rh-S	98.32(5)	Rh-S-Rh'	72.42(4)
P-Rh-S'	166.55(5)	Rh-S-C(2)	87.10(15)
P-Rh-C(1)	100.49(12)	Rh'-S-C(2)	86.07(15)
S-Rh-S'	71.03(6)	Rh-C(1)-Rh'	91.3(3)
S-Rh-C(1)	88.73(14)	Rh-C(1)-O	134.36(16)

Primed atoms are related to the unprimed ones by the symmetry transformation $-x, y, \frac{1}{2}-z$.

The structural parameters of compound **7** calculated by DFT show a good agreement with those obtained experimentally. In particular, the calculated Rh-Rh distance is $2.923\text{\AA}$ (experimental $2.8230(9)\text{\AA}$) whereas the Rh-C-Rh angle around the bridging carbonyl ligand is 95.0° (experimental $91.3^\circ(3)$). The NPA charges on the rhodium atoms are $+0.13$ (Table 5) which are similar to those found on the

formally acetyl bonded Rh(III) centers in compounds **5** and **6**. The assignment of a formal Rh(III) oxidation state would require a bridging carbonyl with a full ketonic character (CO^{2-}), however, the geometric parameters (CO bond distance of 1.181 Å, and a Rh-C-Rh bond angle of 95.0°) and the NPA analysis point to an usual bridging carbonyl. On the other hand, the alternative description of **7** as a dinuclear Rh(II)-Rh(II) species composed of 18 e⁻ metal centers linked by a double metal-metal bond, in order to satisfy the EAN rule, seems to be unrealistic on the basis of the WBI index calculations. The Rh-Rh WBI index of 0.142 denotes only a single metal-metal bond in **7**, which is probably weakened by the presence of the bridging carbonyl. In this context, a comparison with the related compound lacking a bridging carbonyl $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{I})_2(\text{CO})_2(\text{PPh}_3)_2]$ (**8**) (see below) is certainly informative (Table 5). The WBI index in compound **8**, where a single Rh-Rh bond can be invoked on the basis of the EAN rule, is 0.253. Thus, the small value of 0.142 for **7** reflects the usual role of the bridging carbonyl lowering the strength of the metal-metal interaction and, giving the net charge of the bridging carbonyl ligand of +0.002, rule out the presence of a formal Rh-Rh double bond in **7**.

The bonding scheme in the “ $\text{Rh}_2(\mu\text{-CO})\text{P}_2$ ” subunit of **7** is closely related to the described for the *early-late* heterobimetallic compound **4**. In fact, the natural charges on the rhodium centers and the similar WBI indexes for the Rh-Rh and CO bonds in both compounds strongly suggest the presence of electronically unsaturated metal centers bridged by a carbonyl ligand with no ketonic character and a significant metal-metal interaction. The main difference between both complexes is the natural charge on the rhodium atoms that is slightly higher in **4** (0.20 vs 0.13). This fact probably reflects the electronic influence of the *early* metal center reducing the electron-donating ability of the sulfido ligands compared to the alkyl-thiolato ligands.

The ^1H NMR spectrum of **7** in C_6D_6 features an AB quartet at δ 3.33 ppm ($J_{\text{AB}} = 14.6$ Hz) for the benzylic protons of the *gem*-dithiolato ligand in full agreement with the C_2 symmetry structure found in the solid state. In addition, the equivalent triphenylphosphino ligands were observed as a doublet at

δ 39.41 ppm ($J_{\text{Rh-P}} = 148.20$ Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

Table 5. Relevant natural charges and Wiberg bond indexes (WBI) obtained by NBO analysis in *gem*-dithiolato-bridged dinuclear rhodium complexes **7** and **8**.

Compound	Natural charges	WBI
7	Rh ¹ (0.132)	Rh ¹ -Rh ² (0.142)
	Rh ² (0.131)	Rh ¹ C ^μ (0.693)
	C ^μ (0.502)	Rh ² C ^μ (0.696)
	O ^μ (-0.500)	C ^μ O ^μ (1.932)
8	Rh ¹ (0.088)	Rh ¹ -Rh ² (0.253)
	Rh ² (0.033)	Rh ¹ C ¹ (0.611)
	C ¹ (0.491)	C ¹ O ¹ (2.163)
	O ¹ (-0.429)	Rh ² C ² (0.789)
	C ² (0.544)	C ² O ² (2.105)
	O ² (-0.456)	

Complex **7** has only a precedent in the literature: the dinuclear pyrazolato complex $[\text{Rh}_2(\mu\text{-}3,5\text{-Me}_2\text{Pz})_2(\text{I})_2(\mu\text{-CO})(\text{PPh}_3)_2]$ ²⁸ that was obtained by reaction of $[\text{Rh}(\mu\text{-}3,5\text{-Me}_2\text{Pz})(\text{I})(\text{CO})(\text{PPh}_3)]_2$ with 1,2-diiodoethane. However, the Rh···Rh separation of 3.20 Å in this compound is markedly longer than that found in **7**.

In order to know the relationship between complexes **6** and **7**, the reaction of **3** with MeI was investigated by $^{31}\text{P}\{^1\text{H}\}$ NMR at different reaction times. Compound **6** is the major species (>95%) after 1 hour with trace amounts of **7** along with an unknown oxidized species (δ 28.25 ppm, $J_{\text{Rh-P}} = 124.0$ Hz). However, after 6 hours the composition of the reaction mixture is: **6** (50%), **7** (25%) and the oxidized species (25%), assuming a dinuclear formulation for the latter. Compound **7** was obtained as brown crystals in 16% from this solution. Longer reaction times evidenced the conversion of **6** into **7**

although and increase the amount of the oxidized species and the formation of other unidentified species was also observed. Thus, the formation of **7** from **6** likely involves the oxidative addition of MeI at the Rh(I) center of **6** followed by acetone elimination (Scheme 4).²⁹

Scheme 4

Reaction of $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (3**) with I_2 .** Compound **3** reacted with molecular iodine in dichloromethane to give a mixture of the dinuclear compounds $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{I})_2(\mu\text{-CO})(\text{PPh}_3)_2]$ (**7**) and $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{I})_2(\text{CO})_2(\text{PPh}_3)_2]$ (**8**) in a 40:60 ratio (Scheme 5). Compound **8**, the expected transannular oxidative addition product, has been characterized spectroscopically in the reaction mixture. The dinuclear formulation of **8** is supported by the FAB+ mass spectrum. In addition, the IR spectrum shows a broad $\nu(\text{CO})$ band at 2037 cm^{-1} for the terminal carbonyl ligands consistent with a two-center oxidative addition of I_2 with concurrent formation of a Rh-Rh bond. The observed shift to higher frequency of the terminal carbonyl stretching $\nu(\text{CO})$ band relative to **3**, $\Delta\nu$ of 70 cm^{-1} , is in the expected range for the formation of a Rh(II)-Rh(II) dimer.^{7a, 9e, 10d} The $^{31}\text{P}\{^1\text{H}\}$ NMR in C_6D_6 shows two doublets of doublets at δ 39.41 and 15.20 ppm with $J_{\text{Rh-P}}$ coupling constants of 119.7 and 123.4 Hz, respectively, and a mutual $J_{\text{P-P}}$ coupling of 26.0 Hz, indicative of the presence of two inequivalent PPh_3 ligands. In addition, the ^1H NMR spectrum features four doublet resonances between δ 5.29 and 2.53 ppm ($J_{\text{H-H}} = 16.1$ and 13.9 Hz) for the benzylic protons of the *gem*-dithiolato bridging ligand, in agreement with the lack of symmetry of the molecule.

The asymmetric structure of **8** most likely arises from the relative disposition of the added iodido

ligands in the dinuclear structure. In general, the transannular oxidative addition of iodine is stereoselective giving the isomer having the two added iodine atoms with a nearly *trans* disposition relative to the metal-metal bond,³⁰ with the only exception found being the compound $[\text{Rh}_2(\mu\text{-}1,8\text{-(NH)}_2\text{naphth})(\text{I})_2(\text{CO})_2(\text{PPh}_3)_2]$ where a iodo and triphenylphosphine ligands are located *trans* to the Rh-Rh bond.^{31, 32} The proposed structure for **8**, with an iodo and carbonyl ligands *trans* to the Rh-Rh bond, is the most likely if the steric influence of the benzyl substituents of the the *gem*-dithiolato bridging ligand is taken into consideration (Scheme 5).

Monitoring of the reaction mixture by $^{31}\text{P}\{^1\text{H}\}$ NMR evidenced the high stability of **8** which allow us to discard the decarbonylation of **8** as a pathway for the formation of **7**. Instead, we have found that complex **7** slowly decomposes in solution to unidentified species. In fact, the ratio between both complexes changed to 20:80 after 3 days at room temperature and, as expected, the decomposition of **7** is faster at higher temperature. Thus, the formation of **7** should result from the decarbonylation of an intermediate species in route to **8**. This observation contrast with the behavior of the metal-metal bonded dinuclear pyrazolato Rh(II)-Rh(II) complex $[\text{Rh}(\mu\text{-}3,5\text{-Me}_2\text{Pz})(\text{I})(\text{CO})(\text{PMe}_2\text{Ph})]_2$ that slowly transforms (several days) into $[\text{Rh}_2(\mu\text{-}3,5\text{-Me}_2\text{Pz})_2(\text{I})_2(\mu\text{-CO})(\text{PMe}_2\text{Ph})_2]$ with the loss of coordinated CO.²⁸

Scheme 5. Oxidative addition of I_2 to *gem*-dithiolato-bridged dinuclear rhodium complexes.

Reaction of $[\text{Cp}^{\text{t}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(\text{CO})\}_2(\mu\text{-dppm})]$ (1**) with I_2 .** The heterotrinnuclear ZrRh_2 core of **1** breaks down by reaction with molecular iodine. Reaction of **1** with 1 equiv of iodine in dichloromethane gave a dark red solution in 30 min. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the brown solid obtained from this solution evidenced the formation of a complex mixture of compounds. However, reaction with an excess of iodine (3 equiv) resulted in the formation of the mononuclear compound $[\text{Cp}^{\text{t}}_2\text{ZrI}_2]$,³³ which was extracted from the reaction crude with *n*-hexane, and a sparingly soluble dark brown material. This solid could not be fully characterized although is believed to be a dinuclear species of the type $[\{\text{Rh}(\text{CO})\}_2(\mu\text{-S})_n(\mu\text{-dppm})(\text{I})_m]$. The $^{31}\text{P}\{^1\text{H}\}$ NMR in CDCl_3 showed a complex resonance at δ 25.69 ppm, typical of an AA'XX' spin system ($\text{A} = ^{31}\text{P}$ y $\text{X} = ^{103}\text{Rh}$), that has been simulated with the following coupling constants: $^1J_{\text{Rh-P}} = 136.82$ Hz, $^2J_{\text{P-P}} = 9.11$ Hz and $^3J_{\text{Rh-P}} = -2.95$ Hz. On the other hand, the two $\nu(\text{CO})$ bands at 2054 (vs), 2038 (sh) cm^{-1} observed in IR spectrum for the terminal carbonyl ligands and the magnitude of the $J_{\text{Rh-P}}$ coupling constant support a dimeric structure with Rh(III) centers.

Reaction pathway for the formation of $[\text{Cp}^{\text{t}}_2\text{Zr}(\mu_3\text{-S})_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-dppm})(\text{I})(\text{COCH}_3)]$ (4**).** It has been established both theoretically and experimentally, that the oxidative addition of MeI to square-planar d^8 metal complexes proceeds via a two-step mechanism involving a $\text{S}_{\text{N}}2$ nucleophilic attack by the d^8 metal ion on MeI followed by I^- coordination to Rh(III). This mechanism can be also operative in dinuclear complexes as it has been recently shown by DFT calculations on a molecular model of the Freixa's $[\text{Rh}_2(\mu\text{-Cl})_2(\text{SPAN-PPh}_2)(\text{CO})_2]$ methanol carbonylation catalyst where a linear arrangement of the $\text{I-CH}_3\text{-Rh}$ moiety was identified.³⁴ An alternative mechanism involving free alkyl radical intermediates seems to be less likely as the reaction also takes place in the dark and no side reactions were observed.³⁵

The mechanism for the formation of complex **4** has been studied computationally by means of DFT calculations. In spite of the size of our system, that has prevented a detailed mechanistic study, we have

tried to shed some light into the sequence of steps followed from the initial methylation to the final carbonyl bridged acetyl complex.

We have used different complexity levels in the description of the thiolato bridging system of the dinuclear entity, but maintaining always the “Rh₂(μ-dppm)” core modeled as “Rh₂{μ-CH₂(PH₂)₂}”. The thiolato bridge has been modeled starting from a simple S₂CH₂ (model **a**), then changing to Cp₂ZrS₂ (model **b**) and eventually to the actual *early* metalloligand bridge (tBu₂Cp)₂ZrS₂ (model **c**) (Table 6). This approach intends to understand the steric and electronic role of the thiolato bridge on the behavior of the dinuclear Rh₂ core towards CH₃I oxidative addition. Assuming that the oxidative addition reaction has a similar initial methylation step than those of CH₃I in mononuclear rhodium complexes leading to cationic intermediate methyl-complexes, the question arises whether this step is followed by carbonyl insertion, to form the final acetyl group, or by the coordination of I⁻ to the second rhodium atom.

In all the three models the cationic acetyl species is less stable than the cationic methyl-rhodium analogue although the more sterically congested having the bulky *early* metalloligand as bridge (model **c**) shows the lesser relative instability (13.4 kcal·mol⁻¹). This difference is significantly reduced after coordination of the iodide ion to the second rhodium atom leading to the metal-metal bonded Rh(II) species. The energy difference between the methyl and acetyl complexes is only 1.4 kcal/mole for model **a**, and interestingly is shifted in favor of the acetyl isomer for models **b** and **c** by 7.4 and 4.1 kcal·mol⁻¹, respectively. According to these energies the carbonyl insertion step must occur after coordination of I⁻ to the second rhodium center.

A second aspect to be considered is the stability of the carbonyl bridged acetyl species. Although this species is the least stable isomer for all the three models, it becomes more stable when going from the simple bridging model **a** to the more congested model **c** (+16.5, 9.3 and 6.0 kcal·mol⁻¹, respectively). The optimization of the full molecules (without solvent effects) reduces this difference to 2.4 kcal·mol⁻¹. Thus, the formation of the bridging carbonyl must occur at the same time or after coordination of the

iodide ion as the cationic species are all at a much higher energy.

Table 6. Relative energies (kcal mol⁻¹) of the potential neutral and cationic intermediates in the MeI oxidative addition on **1** leading to the formation of **4** showing the influence of the bridging B group.

<div style="display: flex; align-items: center; justify-content: center;"> <div style="writing-mode: vertical-rl; transform: rotate(180deg);">Intermediate</div> <div style="margin-left: 10px;">B group</div> </div>	model a	model b	model c
	model a	model b	model c
0.0	7.4	4.1
1.4	0.0	0.0
16.5	9.3	6.0
0.0	0.0	0.0
19.1	14.3	13.4
35.6	31.9	29.3

^a The binuclear rhodium core “Rh₂(CO)₂(μ-dppm)” has been modeled as “Rh₂(CO)₂{μ-CH₂(PH₂)₂}”

The results obtained from the DFT calculations suggest the initial formation of the metal-metal

bonded iodo-methyl species as a result of the MeI oxidative addition (S_N2 mechanism). In a second step, a metal-metal bonded iodo-acetyl species, $[\text{Cp}^t\text{Zr}(\mu_3\text{-S})_2\text{Rh}_2(\mu\text{-dppm})(\text{CO})(\text{I})(\text{COCH}_3)]$, should be formed by migratory insertion of the carbonyl ligand into the Rh-Me bond. Finally, compound **4** should result from an oxidative isomerization in which the terminal carbonyl ligand inserts into the rhodium-rhodium bond.^{10a} The steric interference of the bulky *t*-Bu groups on the metalloligand and the iodo ligand in the axial position in the metal-metal bonded iodo-acetyl species is the driving force for this transformation that ends up with the iodo ligand *cis* to the Rh-Rh vector. The oxidative isomerization has been found to be reversible in A-frame pyrazolate-bridged dirhodium complexes, which suggests that the process requires a low energy input.³⁶

Scheme 6. Concerted mechanism proposed for the oxidative addition of MeI on **1** leading to **4**.

Nevertheless, the DFT calculations are also in agreement with a concerted mechanism, which is shown in Scheme 6. Most probably, the steric pressure exerted by the metalloligand has a pivotal role in promoting the oxidative isomerization process after coordination of the iodide anion on the second rhodium center. At the same time, the bridging ketonic carbonyl facilitates the migratory carbonyl

insertion into the Rh-Me bond leading to the formation of the acetyl moiety.

Concluding Remarks

The structurally related dinuclear *gem*-dithiolato bridged rhodium complexes $[\text{Rh}_2(\mu\text{-S}_2\text{CR}_2)(\text{CO})_2(\text{PPh}_3)_2]$ and the *early-late* $d^0\text{-}d^8$ sulfido-bridged cluster $[\text{Cp}^{\text{tt}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Rh}(\text{CO})\}_2(\mu\text{-dppm})]$ have allowed for a comparative study of their reactivity to determine the influence of the *early* metallocene fragment on the outcome of the oxidative addition reactions. In fact, the *gem*-dithiolato bridged complexes can be considered as the “carbon” equivalents of the trigonal-bipyramidal core $[\text{ZrRh}_2(\mu_3\text{-S})_2]$ in the heterometallic cluster. The *gem*-dithiolato complexes behave similarly to the dinuclear complexes having thiolato bridging ligands, $[\text{Rh}(\mu\text{-SR})(\text{CO})(\text{PR}_3)]_2$. The oxidative addition of MeI gives a Rh(III)-Rh(I) acetyl compound that arise from a one-center MeI oxidative addition followed by methyl migration. However, the reaction with molecular iodine is unselective and results in the formation of the asymmetric Rh(II)-Rh(II) transannular oxidative addition product and the unusual compound $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{I})_2(\mu\text{-CO})(\text{PPh}_3)_2]$ having only a bridging carbonyl ligand. Most probably, the latter results from the decarbonylation of an intermediate species in route to the former.

In sharp contrast, the heterotrinnuclear ZrRh_2 core of the cluster breaks down in the reaction with molecular iodine as was evidenced by the isolation of the mononuclear compound $[\text{Cp}^{\text{tt}}_2\text{ZrI}_2]$. However, the oxidative addition of methyl iodide affords the unusual heterobimetallic compound $[\text{Cp}^{\text{tt}}_2\text{Zr}(\mu_3\text{-S})_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-dppm})(\text{I})(\text{COCH}_3)]$ showing a formally Rh(III)-Rh(III) subunit with iodido and acetyl as terminal ligands, and a diphosphine and a carbonyl as bridging ligands. The mechanism for the formation of this compound has been studied by DFT calculations with increasing complexity in the dithiolato system bridging the dinuclear rhodium core. The obtained results suggest that the electronic and steric effects imparted by the *early* “ $\text{Cp}^{\text{tt}}_2\text{Zr}$ ” fragment attached to the dinuclear rhodium unit account for this oxidative addition product that has no precedent in dinuclear rhodium or iridium

chemistry. The oxidative addition of MeI seems to proceed more likely via a two-step mechanism involving a S_N2 nucleophilic attack by a Rh(I) center on MeI followed by I⁻ coordination to the adjacent rhodium center. The steric influence of the “Cp^{tt}₂Zr” fragment enforce, in a concerted way, the migration of the carbonyl ligand to the bridge position breaking the Rh-Rh bond (oxidative isomerization) and the migratory insertion of the adjacent carbonyl leading to the formation of the acetyl moiety.

Experimental Section

General Methods. All manipulations were performed under a dry argon atmosphere using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. The compounds [Cp^{tt}₂Zr(SH)₂],^{14b} [Cp^{tt}₂Zr(μ₃-S)₂{Rh(CO)₂}(μ-dppm)] (**1**),^{14a} [Rh₂(μ-S₂Cy)(CO)₂(PPh₃)₂] (**2**)¹³ and [Rh₂(μ-S₂CBn₂)(CO)₂(PPh₃)₂] (**3**)¹² were prepared as described previously. [{Rh(μ-Cl)(cod)}₂] was prepared following the literature procedure.³⁷ Benzyltriphenylphosphonium chloride and ¹³CO were obtained from Aldrich and Isotec respectively.

Physical Measurements. ¹H, ³¹P{¹H} and ¹³C{¹H} NMR spectra were recorded on a Varian Gemini 300 (300.08, 121.47 and 75.46 MHz), Bruker Avance 300 (300.13, 121.50 and 75.48 MHz) or Bruker Avance 400 (400.13, 161.99 and 100.61 MHz). Chemical shifts are reported in parts per million and referenced to SiMe₄ using the signal of the deuterated solvent (¹H and ¹³C) and 85% H₃PO₄ (³¹P) as external reference respectively. Assignments in complex NMR spectra were done by simulation with the program gNMR v 3.6 (Cherwell Scientific Publishing Limited) for Macintosh. The initial choice of chemical shifts and coupling constants were optimized by successive iterations following a standard least-squares procedure, a numerical assignment of the experimental frequencies was used. IR spectra were recorded on a Nicolet-IR 550 spectrometer using a cell with NaCl windows. C, H and N analysis were performed in a Perkin-Elmer 2400 CHNS/O microanalyzer. Conductivities were measured in ca.

$5 \cdot 10^{-4}$ M acetone solutions using a Philips PW 9501/01 conductimeter. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB⁺ mode. Ions were produced with the standard Cs⁺ gun at ca. 30 Kv, 3-nitrobenzyl alcohol (NBA) was used as matrix. Electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTof-Q using sodium formate as reference.

Synthesis of the complexes. **[Cp^u₂Zr(μ₃-S)₂{Rh(¹³CO)₂}]₂**. A suspension of [{Rh(μ-Cl)(cod)}₂] (0.100 g, 0.203 mmol) in a dichloromethane/methanol (1 ml/10 ml) solution of [PPh₃Bz]Cl (0.158 g, 0.407 mmol) was prepared in a 50 ml Schlenk tube. The Schlenk was evacuated and charged with 1 atm of ¹³CO and the suspension stirred for 25 min at room temperature to give a clear pale yellow solution. NEt₃ (60 μl, 0.432 mmol), solid [Cp^u₂Zr(SH)₂] (0.104 g, 0.203 mmol) and diethyl ether (3 ml) were quickly and successively added. The solution immediately turned green and an emerald-green solid started to precipitate. After stirring for 15 min the Schlenk tube was flushed with argon and the solid filtered, washed with methanol (2 x 5 ml) and diethyl ether (5 ml), and dried under vacuum. Yield: 0.132 g, 0.159 mmol, 78%. IR (CH₂Cl₂, cm⁻¹): ν(CO), 2016 (s), 1994 (s), 1950 (s) cm⁻¹.

[Cp^u₂Zr(μ₃-S)₂Rh₂(μ-CO)(μ-dppm)(I)(COCH₃)] (4). [Cp^u₂Zr(μ₃-S)₂{Rh(CO)}₂(μ-dppm)] (**1**) (0.242 g, 0.209 mmol) was dissolved in neat MeI (5 mL) to give a brown red solution in less than 5 min. The solution was stirred for 30 min and then n-hexane (10 mL) was added. Concentration of the resulting suspension under vacuum to ca. 5 mL gave the compound as a microcrystalline dark brown-red solid which was isolated by filtration, washed twice with n-hexane (5 mL) and dried under vacuum. Yield: 0.254 g, 0.196 mmol, 93%. Anal. Calcd for C₅₄H₆₇IO₂P₂Rh₂S₂Zr: C, 49.96; H, 5.20; S, 4.94. Found: C, 49.73; H, 5.83; S, 4.68. MS (FAB⁺, CH₂Cl₂, m/z): 1225 (M⁺ - 2CO - CH₃, 100%), 1141 (M⁺ - CO - I, 17%), 1113 (M⁺ - 2CO - I, 19%), 1098 (M⁺ - 2CO - I - CH₃, 28%), 1063 (M⁺ - Cp^u - 2CO, 9%), 1048 (M⁺ - Cp^u - 2CO - CH₃, 13%). ¹H NMR (300.08 MHz, CDCl₃, 293 K): δ 8.0-6.80 (m, 20H, dppm), 6.50, 6.47, 6.33, 6.07, 5.88 and 5.83 (t, J_{p-H} = 2.6 Hz, 1H each, H₂, H₄ and H₅, Cp^u), 3.10-2.84 (m, 2H,

>CH₂ ppm), 2.44 (br s, 3H, COCH₃), 1.38, 1.36, 1.34 and 1.05 (br s, 9H each, CH₃, Cp^{tt}). ¹³C{¹H} NMR (75.46 MHz, CDCl₃, 293 K, carbonyl region): δ 232.09 (dd, COCH₃), 217.81 (m, CO). ³¹P{¹H} NMR (121.47 MHz, CDCl₃, 293 K): δ 28.3 (m, spin system, see text). IR (CH₂Cl₂, cm⁻¹): ν(CO), 1788 (s, br).

[Cp^{tt}₂Zr(μ₃-S)₂Rh₂(μ-¹³CO)(μ-dppm)(I)(¹³COCH₃)] (4*). An NMR tube was charged with [Cp^{tt}₂Zr(μ₃-S)₂{Rh(¹³CO)₂}₂] (0.025 g, 0.030 mmol), dppm (0.012 g, 0.031 mmol) and CDCl₃ (0.4 mL) to give a dark green solution of the complex [Cp^{tt}₂Zr(μ₃-S)₂{Rh(¹³CO)₂}₂(μ-dppm)] (1*). Addition of MeI (60 μL, 0.935 mmol) and heating at 50 °C for 5 min gave a red brown solution of 4*.

[Rh₂(μ-S₂Cy)(CH₃CO)(I)(CO)(PPh₃)₂] (5). An orange solution of [Rh₂(μ-S₂Cy)(CO)₂(PPh₃)₂] (2) (0.190 g, 0.204 mmol) in neat MeI (2 mL) was stirred for 1 hour at room temperature to give a dark red solution. The solvent was removed under vacuum and the brown residue dissolved in the minimum volume of benzene. Slow addition of diethyl ether gave the compound as a brown-red microcrystalline solid that was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.190 g, 0.177 mmol, 87 %. Anal. Calcd for C₄₅H₄₃IO₂P₂Rh₂S₂: C, 50.30; H, 4.03; S, 5.97. Found: C, 50.21; H, 3.98; S, 5.57. MS (ESI⁺, CH₃CN, m/z): 947.0 (M⁺ - I). MS (ESI⁺, C₆H₆, m/z): 1058.8 (M⁺ - CH₃), 947.0 (M⁺ - I). ¹H NMR (300.13 MHz, CD₂Cl₂, RT): δ 7.77–7.70 (m, 12H), 7.48–7.42 (m, 12H), 7.20 (br, 6H) (PPh₃), 3.30 (s, 3H, CH₃CO), 2.62 (m, 2H), 2.31 (m, 2H), 2.02 (m, 2H), 1.80 (m, 2H), 0.89 (m, 2H) (>CH₂). ¹³C{¹H} NMR (75.48 MHz, CD₂Cl₂, RT): δ 216.9 (dd, CH₃CO, J_{Rh-C} = 25.3 Hz, J_{P-C} = 5.7 Hz), 188.3 (dd, CO, J_{Rh-C} = 76.8 Hz, J_{P-C} = 16.8 Hz), 135.4 (br), 134.7 (d, J_{Rh-P} = 12 Hz), 134.1 (d, J_{Rh-P} = 46 Hz), 131.0, 130.9, 129.2 (d, J_{Rh-P} = 10 Hz), 128.4 (d, J_{Rh-P} = 10 Hz) (PPh₃), 86.8 (C₁), 57.4 (C₂ or C₆), 51.0 (CH₃CO), 47.2 (C₂ or C₆), 25.6 (C₄), 23.1, 21.5 (C₃ and C₅). ³¹P{¹H} NMR (121.50 MHz, CD₂Cl₂, RT): δ 38.41 (dd, J_{Rh-P} = 158.1 Hz, J_{P-P} = 5.0 Hz), 37.62 (dd, J_{Rh-P} = 146.0 Hz, J_{P-P} = 5.0 Hz). IR (CH₂Cl₂, cm⁻¹): ν(CO), 1985 (s), 1683 (s).

[Rh₂(μ-S₂CBn₂)(CH₃CO)(I)(CO)(PPh₃)₂] (6). [Rh₂(μ-S₂CBn₂)(CO)₂(PPh₃)₂] (**3**) (0.230 g, 0.220 mmol) was dissolved in neat MeI (2 mL) and stirred for 1 hour at room temperature. The resulting dark red solution was brought to dryness under vacuum and the residue dissolved in dichloromethane (1 mL). Slow addition of diethyl ether gave the compound as a brown-red microcrystalline solid, which was filtered, washed with diethyl ether, and dried under vacuum. Yield: 0.220 g, 0.185 mmol, 84%. Anal. Calcd for C₅₄H₄₇IO₂P₂Rh₂S₂: C, 54.65; H, 3.99; S, 5.40. Found: C, 54.69; H, 3.59; S, 5.69. MS (ESI⁺, CH₂Cl₂, m/z): 1059.0 (M⁺ - I). ¹H NMR (400.13 MHz, CD₂Cl₂, RT): δ 7.86 (m, 4H), 7.73 (m, 8H), 7.51–7.20 (set of m, 18H) (PPh₃), 7.24 (m, 2H), 7.15 (m, 2H), 7.10 (m, 2H), 7.07 (m, 2H), 6.98 (m, 2H) (Ph), 4.35 (d, 1H, J_{H-H} = 14.9 Hz, >CH₂), 3.34 (d, 1H, J_{H-H} = 14.6 Hz, >CH₂), 3.29 (s, 3H, CH₃CO), 3.05 (d, 1H, J_{H-H} = 14.9 Hz, >CH₂), 2.83 (d, 1H, J_{H-H} = 14.6 Hz, >CH₂). ¹³C{¹H} NMR (75.48 MHz, CD₂Cl₂, RT): δ 218.3 (ddd, CH₃CO-, J_{Rh-C} = 25.3 Hz, J_{P-C} = 5.5 Hz, J_{P-C} = 0.3 Hz), 187.8 (dd, CO, J_{Rh-C} = 76.8 Hz, J_{P-C} = 17.2 Hz, CO), 136.3, 135.8 (Ph), 134.5 (d, J_{Rh-C} = 12 Hz, PPh₃), 134.5 (d, J_{Rh-C} = 12 Hz), 133.5 (d, J_{Rh-C} = 47 Hz) (PPh₃), 131.1, 130.87, 130.84, 130.65 (Ph), 130.63, 128.8 (d, J_{Rh-C} = 12 Hz) (PPh₃), 128.3, 128.3, 128.2, 128.1, 127.1, 127.0 (Ph), 87.0 (CS₂), 59.6 (>CH₂, Bn), 51.2 (CH₃CO), 49.8 (>CH₂, Bn₂). ³¹P{¹H} NMR (121.50 MHz, C₆D₆, RT): δ 38.30 (dd, J_{Rh-P} = 145.6 Hz, J_{P-P} = 4.9 Hz), 37.45 (dd, J_{Rh-P} = 156.7 Hz, J_{P-P} = 4.9 Hz). IR (CH₂Cl₂, cm⁻¹): ν(CO), 1988 (s), 1682 (s).

[Rh₂(μ-S₂CBn₂)(I)₂(μ-CO)(PPh₃)₂] (7). Compound **3** (0.050 g, 0.048 mmol) was reacted with MeI for 6 hours following the procedure described above. The solution was brought to dryness and the residue dissolved in CH₂Cl₂ (2 ml), layered with diethyl ether and kept at room temperature for several days. The brown crystals were filtered off, washed with pentane and dried in vacuo. Yield: 0.010 g, 0.008 mmol, 16 %. Anal. Calcd for C₅₅H₅₀Cl₆I₂OP₂Rh₂S₂ (**7** · 3CH₂Cl₂): C, 43.31; H, 3.30; S, 4.20. Found: C, 43.35; H, 3.35; S, 4.35. ¹H NMR (400.13 MHz, C₆D₆, RT): δ 8.00 (m, 12H), 7.31 (m, 4H), 7.15 (m, 12H), 7.07 (m, 12H) (PPh₃ and Ph), 3.33 (AB q: δ_A = 3.47, δ_B = 3.18, J_{AB} = 14.6 Hz, 4H, >CH₂).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.50 MHz, C_6D_6 , 293 K): δ 39.41 (d, $J_{\text{Rh-P}} = 148.20$ Hz). IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO})$, 1675 (m). MS (FAB $^+$, C_6D_6 , m/z): 1016 ($\text{M}^+ - 2\text{I}$, 20%), 889 ($\text{M}^+ - \text{PPh}_3 - \text{CO} - \text{Bn}$, 32%).

Reaction of $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{CO})_2(\text{PPh}_3)_2]$ with I_2 . A solution of I_2 (0.037 g, 0.145 mmol) in dichloromethane (2 mL) was slowly added to a solution of $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (**3**) (0.150 g, 0.144 mmol) in dichloromethane (3 mL). The solution was stirred for 30 min to give a dark brown solution. This solution was concentrated under vacuum and then *n*-hexane was added to give a dark orange-brown solid that was filtered, washed with *n*-hexane and dried under vacuum (0.177 g). The isolated solid is a mixture of complexes **7** and **8** in 40:60 ratio (determined by NMR). NMR, MS and IR data for $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{I})_2(\text{CO})_2(\text{PPh}_3)_2]$ (**8**): ^1H NMR (300.13 MHz, C_6D_6 ; 293 K): δ 8.2–6.6 (set of m, Ph, PPh_3 and S_2CBn_2), 5.29 (d, 2H, $>\text{CH}_2$, $J_{\text{H-H}} = 13.9$ Hz), 4.20 (d, 2H, $>\text{CH}_2$, $J_{\text{H-H}} = 13.9$ Hz), 3.23 (d, 1H, $>\text{CH}_2$, S_2CBn_2 , $J_{\text{H-H}} = 16.1$ Hz), 2.53 (d, 1H, $>\text{CH}_2$, $J_{\text{H-H}} = 16.1$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.50 MHz, C_6D_6 , 293 K): δ 39.41 (dd, $J_{\text{Rh-P}} = 119.7$ Hz; $J_{\text{P-P}} = 26.0$ Hz), 15.20 (dd, $J_{\text{Rh-P}} = 123.4$ Hz; $J_{\text{P-P}} = 26.0$ Hz). IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO})$, 2037 (m). MS (FAB $^+$, C_6D_6 , m/z): 1171 ($\text{M}^+ - \text{I}$, 12%), 1016 ($\text{M}^+ - \text{CO} - 2\text{I}$, 20%), 889 ($\text{M}^+ - 2\text{CO} - \text{Bn} - \text{PPh}_3$, 32%).

Theoretical calculations. Structures of compounds **2-7** and **8** were fully optimized using the Gaussian 09 software package³⁸ at the density functional level of theory (DFT) with the B3LYP functional. Several models were used for the study of the oxidative addition of ICH_3 , as shown in Table 6. The lanl2dz basis set and ECP was used for Rh and I atoms and the 6-31G** basis set for the rest of elements. The structures of the optimized molecules were depicted with the CyLview program.³⁹ The natural charges calculated by natural population analysis (NPA) and the Wiberg bond indexes (WBI) were obtained by NBO analysis with the NBO 5.0 program.¹⁹

Crystal Structure Determination of $[\text{Rh}_2(\mu\text{-S}_2\text{Cy})(\text{CH}_3\text{CO})(\text{I})(\text{CO})(\text{PPh}_3)_2]$ (5**) and $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{I})_2(\mu\text{-CO})(\text{PPh}_3)_2]$ (**7**).** Single crystals for the X-ray diffraction study of **5** (dark red prisms) were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution at 258 K. Crystal of **7** (brown

prisms) were obtained by slow diffusion of diethyl ether into a CH₂Cl₂ solution of the crude mixture obtained from reaction of **3** with MeI for 6 hours. A summary of crystal data, data collection and refinement parameters are provided in the Supporting Information.

Selected crystals were mounted on a Bruker SMART CCD three-circles diffractometer equipped with a graphite monochromator. Data collection was performed at low temperature (100(2) K) using Mo-K α radiation ($\lambda = 0.71073$ Å). A semiempirical absorption correction was applied using SADABS program, as implemented in SAINT-PLUS package.⁴⁰ Both structures were solved by Patterson methods using the program SHELXS-97, completed by subsequent difference Fourier techniques, and refined by full matrix least-squares on F^2 with SHELXL-97.⁴¹ All non-hydrogen atoms were refined with anisotropic displacement parameters. A dichloromethane solvent molecule was observed disordered in the crystal structure of **5**; this molecule was modeled from two moieties with equal occupancies. Three CH₂Cl₂ solvent molecules were also observed in the unit cell of **7**. Hydrogens were included in both structures from calculated positions; in both cases riding positional and thermal parameters were refined.

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Supporting Information Available. X-ray crystallographic files in CIF format for the structure determination of compounds **5** and **7**. Optimized coordinates for compounds **1-8**, and optimized coordinates and energies of the model compounds included in Table 6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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