

Synthesis and Characterization of Single Thiolato-Bridged Heterodinuclear Complexes: Irreversible Isomerization of $\text{Cp}(\text{CO})_2\text{W}(\mu\text{-SPh})(\mu\text{-Cl})\text{Ru}(\text{CO})(\text{Cl})(\text{PPh}_3)$ to $\text{Cp}(\text{CO})(\text{Cl})\text{W}(\mu\text{-SPh})(\mu\text{-Cl})\text{Ru}(\text{CO})_2(\text{PPh}_3)$ via Chloride and Carbonyl Ligand Migration

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Reaction between $\text{CpW}(\text{CO})_3\text{SPh}$ and $\text{RuCl}_2(\text{PPh}_3)_x$ ($x = 3$ and 4) in dichloromethane at room temperature afforded a single thiolato-bridged heterodinuclear complex, $\text{Cp}(\text{CO})_2\text{W}(\mu\text{-SPh})(\mu\text{-Cl})\text{Ru}(\text{CO})(\text{Cl})(\text{PPh}_3)$ (**1**) in high yield. Irreversible isomerization of **1** to $\text{Cp}(\text{CO})(\text{Cl})\text{W}(\mu\text{-SPh})(\mu\text{-Cl})\text{Ru}(\text{CO})_2(\text{PPh}_3)$ (**2**), which exists as a mixture of stereoisomers **2a** and **2b**, occurs via chloride and carbonyl ligand migration during thermolysis of **1** in toluene at $80\text{ }^\circ\text{C}$. Compounds **1**, **2a**, and **2b** were characterized by single-crystal X-ray diffraction analysis. Migration of π -acceptor carbonyl ligands from W atom to Ru atom during the conversion of $\text{CpW}(\text{CO})_3\text{SPh} + \text{RuCl}_2(\text{PPh}_3)_3 \rightarrow \mathbf{1} \rightarrow \mathbf{2}$ with concomitant migration of σ -donor chloride ligand from Ru to W atom in **1** is reported.

Introduction

The dynamic behavior of ligands in fluxional molecules has been well documented in the last three decades¹ and has been observed for organic, inorganic, and organometallic compounds. Among them, ligand migration in organometallic complexes containing metal–metal bonds is of special interest because such occurrence and rationalization are appropriate models for a better understanding of ligand migration in clusters and surface mobility of chemisorbed species.² Ligand migration occurs in different ways, and metal to ligand and metal to metal migrations are more common. Ligands such as acyl,³ alkoxycarbonyl,^{3e} formyl,^{3b,3c} silyl,⁴ germyl,⁵ stannyl,⁵ plumblyl,⁵ hydride,⁶ phosphinate,⁷ and phosphorane⁸ were demonstrated to migrate from a transition metal to the ligand η^5 -cyclopentadienyl ring. In metal

carbonyl compounds, carbonyl migration between metals is very common.¹ However, significantly fewer studies on carbonyl migration on heterometallic clusters than those on homometallic clusters were reported.¹ Furthermore, although the reversible carbonyl ligand migration is usual in metal carbonyl clusters, the irreversible migration of CO ligand from one metal to another metal is less common.⁹

Chloride migration is a unique way to synthesize organic molecules¹⁰ including biological conversion of trichloroethylene to chloral by cytochrome P-450.¹¹ Chloride ion can form a bridging bond in clusters, but its migration on clusters and dinuclear complexes is rare.^{12,13}

Sulfides and phosphines are usual bridging ligands for binding different metals. Thiolato-bridged complexes become more significant over the phosphido-bridged ones when catalytic and

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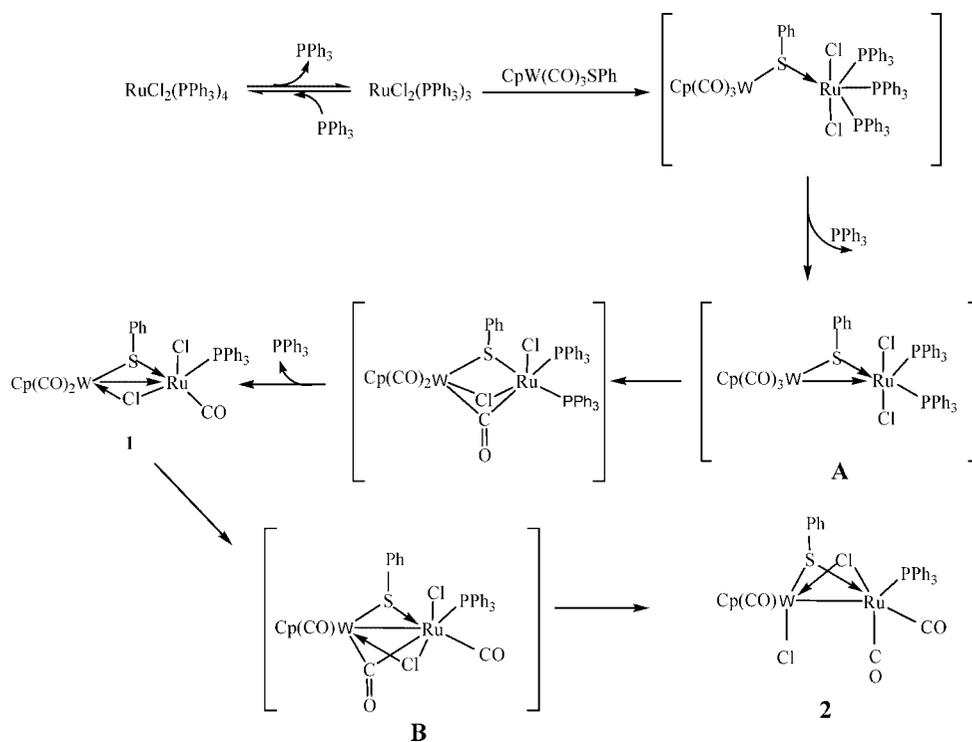
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Scheme 1



biological activities are concerned.¹⁴ Many of them are bimetallic complexes.^{14a14c} The common source of the thiolate ligands in the synthesis of thiolato complexes with M–SR bonding is organic sulfides such as RSH and RSSR.¹⁵ In addition, metallothiolate can transfer thiolate ligand to another metal center and is also used as a thiolate ligand source in the synthesis of thiolato complexes.¹⁶ A vast number of bimetallic compounds containing (μ -SR)₂ bridges were reported.¹⁷ Because only a

small number of heterobimetallic compounds with a single (μ -SR) bridge have been synthesized, the synthesis of such complexes becomes more challenging in chemistry.¹⁸

In continuation of our studies in heterobimetallic complexes,^{16,19} this article reports the synthesis and characterization of two less common single-thiolato-bridged heterobimetallic complexes, Cp(CO)₂W(μ -SPh)(μ -Cl)Ru(CO)(Cl)(PPh₃) (**1**) and Cp(CO)(Cl)W(μ -SPh)(μ -Cl)Ru(CO)₂(PPh₃) (**2**), and a novel intramolecular exchange of carbonyl and chloride ligands between different metal centers (W and Ru) in the conversion of **1** to **2**.

Results and Discussion

Synthesis and Characterization of 1. When a dichloromethane solution of CpW(CO)₃SPh and RuCl₂(PPh₃)₃ was stirred at room temperature for 12 h, the heterodinuclear compound Cp(CO)₂W(μ -SPh)(μ -Cl)Ru(CO)(Cl)(PPh₃) (**1**) was formed in high yield (Scheme 1).

Compound **1** is a 34e heterodinuclear metal–metal bonded compound with a thiolato and a chloride bridge (Figure 1) and is stable both as a solid and in solution. Its structure was characterized by single-crystal X-ray diffraction analysis.

Absorption peaks at 2010 and 1954 cm⁻¹ in the IR spectrum of **1** are assigned to the ν (C≡O) bands of the two terminal carbonyls on W based on the comparison with that of W–CO (2031, 1938 cm⁻¹) of CpW(CO)₃SPh.²⁰ The Ru–CO absorption

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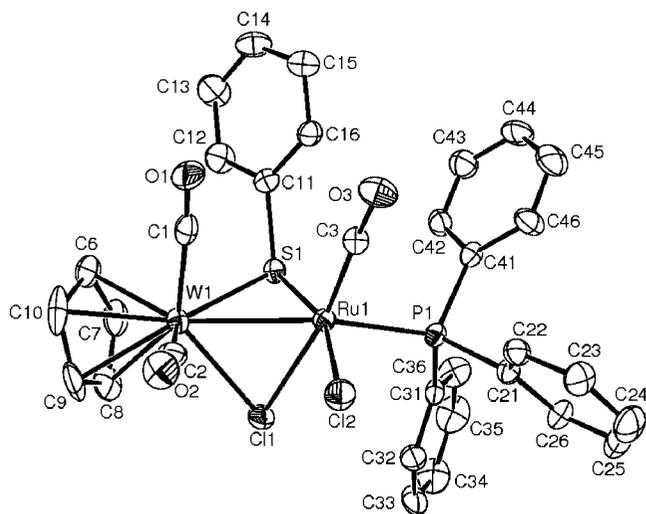


Figure 1. ORTEP drawing of **1**, with 30% thermal ellipsoids. Hydrogen atoms are omitted.

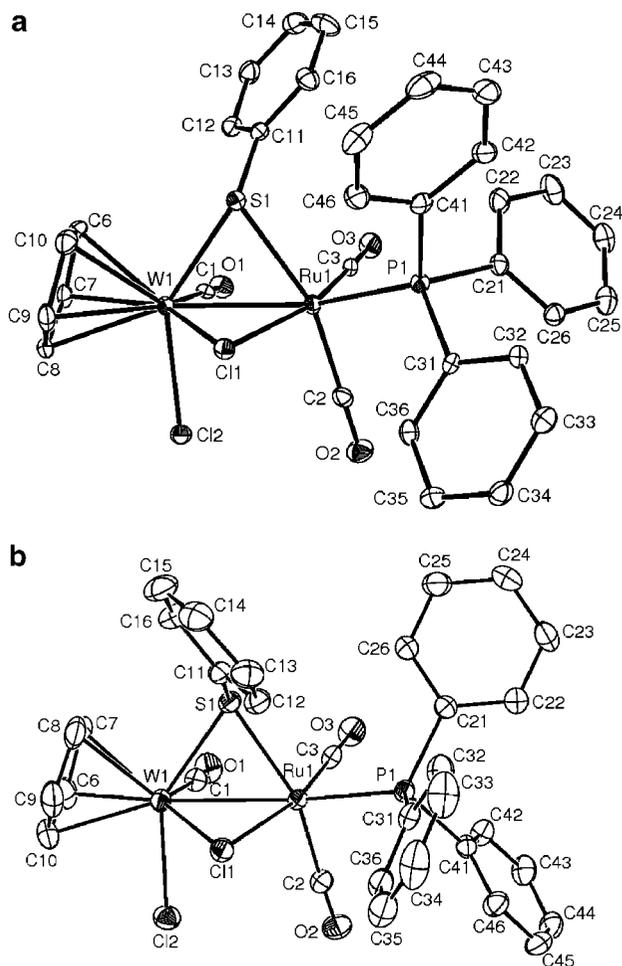


Figure 2. (a) ORTEP drawing of **2a**, with 30% thermal ellipsoids. Hydrogen atoms are omitted. (b) ORTEP drawing of **2b**, with 30% thermal ellipsoids. Hydrogen atoms are omitted.

should be around 1950 cm^{-1} based on the comparison with the $\nu(\text{C}\equiv\text{O})$ bands of Ru–CO ($1948, 1955\text{ cm}^{-1}$) of $(\text{CO})(\text{PPh}_3)\text{Ru}(\mu\text{-Cl})(\mu\text{-SPh})_2\text{Ru}(\text{CO})(\text{PPh}_3)_2$,²¹ and the broad peak at 1954

cm^{-1} in the IR spectrum of **1** could be the superposition of one of the W–CO adsorption peaks and the Ru–CO adsorption peak.

During the formation of **1**, one of the carbonyl ligands on the W site in $\text{CpW}(\text{CO})_3\text{SPh}$ migrates onto the Ru site. It may not be a scrambling reaction because **1** is formed in high yield (93%). Although formal oxidation states of W and Ru in $\text{CpW}(\text{CO})_3\text{SPh}$, $\text{RuCl}_2(\text{PPh}_3)_3$, and **1** are both +2, the migration of the carbonyl ligand is possibly electronic in nature. A possible pathway for the formation of **1** is shown in Scheme 1.

$\text{RuCl}_2(\text{PPh}_3)_3$ is a 16e complex and therefore is a coordinatively unsaturated species. The metathiolate $\text{CpW}(\text{CO})_3\text{SPh}$ can coordinate to the Ru in $\text{RuCl}_2(\text{PPh}_3)_3$ through a lone pair of electrons on the sulfur atom to form a non-metal–metal-bonded 36e dimer, $\text{CpW}(\text{CO})_3(\mu\text{-SPh})\text{RuCl}_2(\text{PPh}_3)_3$, with a $\mu\text{-SPh}$ bridge. A dative metal–metal bond from W to Ru may replace a bulky PPh_3 ligand on Ru, forming the 34e complex

$\text{CpW}(\text{CO})_3(\mu\text{-SPh})\text{RuCl}_2(\text{PPh}_3)_2$ (denoted as **A**) to release the steric hindrance and brings the two metals closer. Through the formation of the dative metal–metal bonding, the Ru in **A** becomes electron rich, and the electron density on W is reduced. This difference in electron density drives the migration of the π -acceptor carbonyl ligand from the electron-deficient W atom²² to the electron-rich Ru atom^{22,23b} to substitute a weak π -acceptor triphenylphosphine ligand through the formation of the bridging chloride to redistribute the electron density of the metals to form **1**.

The reaction of $\text{CpW}(\text{CO})_3\text{SPh}$ and $\text{RuCl}_2(\text{PPh}_3)_4$ under identical conditions also afforded **1** in high yield because triphenylphosphine ligands in both $\text{RuCl}_2(\text{PPh}_3)_4$ and $\text{RuCl}_2(\text{PPh}_3)_3$ are labile. Production of the similar intermediate $\text{RuCl}_2(\text{PPh}_3)_2(\text{solvent})_2$ ²⁴ for both complexes in solvents with weak coordination abilities has been reported.

Thermolysis of 1. After heating at $80\text{ }^\circ\text{C}$, the color of the toluene solution of **1** changed from violet to yellow. Compound **2**, an orange solid, was obtained after chromatography.

The elemental analysis of **2** is similar to that of **1**. This implies that compound **2** has the same empirical formula of **1**. The room-temperature $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra of **2** show two peaks for the triphenylphosphine and the cyclopentadiene ring, respectively, and do not contain signals corresponding to **1**. No $J_{\text{P-W}}$ satellites are observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, showing that the triphenylphosphine ligand is coordinated to Ru. IR of **2** shows three terminal CO absorption peaks, indicating no bridging CO is present, and the pattern of the spectra (both the number of peaks and their positions) is different from that of **1**. All this implies that two isomers (denoted **2a** and **2b**) are present in **2**, and compounds **1** and **2** are constitutional isomers.

The variable-temperature $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra of the compounds indicate that the isomers do not convert to each other in the variable-temperature range of the experiment (65 to $-68\text{ }^\circ\text{C}$) because the ratios of the intensities of triphenylphosphine and cyclopentadiene signals are similar as a function of temperature.²⁵

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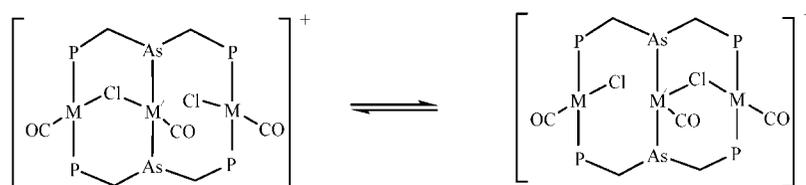
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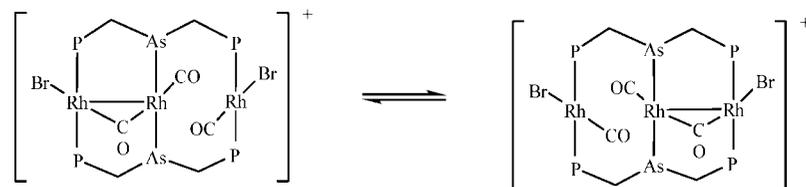
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Chart 1



Bridge/Terminal Halogen Exchange



Bridge/Terminal Carbonyl Exchange

Separation of **2a** and **2b** failed. However, two different types of single crystals of **2** for single-crystal X-ray diffraction analysis were obtained from the same batch of compound **2** by ether diffusion into a dichloromethane solution of **2** at different temperatures. Violet single crystals of **2a** and **2b** were obtained at -4 and -15 °C, respectively, from two sets of crystal growth experiments from the same batch of **2**. The molecular structures of **2a** and **2b** are shown in Figure 2a and b, respectively. Two independent molecules of **2a** were crystallized in the asymmetric unit cell.

Both **2a** and **2b** are 34e heterodinuclear metal–metal bonded compounds with a thiolato and a chloride bridge (Figure 2a and b). The only difference in their structures is the orientation of the lone pair of electrons and the phenyl group on the sulfur atom of the thiolato bridge with respect to the folded RuSCIW core. In **2a**, the phenyl group on sulfur points away from the bridging Cl of the folded RuSCIW core. In **2b**, the orientations of the phenyl group and the lone pair of electrons on sulfur are opposite that of **2a**, with the phenyl group pointing toward and the lone pair of electrons pointing away from the bridging Cl. Thus **2a** and **2b** are stereoisomers.

Two absorption peaks at 2033 and 1971 cm^{-1} in the IR spectrum of **2** are assigned to the $\nu(\text{C}\equiv\text{O})$ bands of the two terminal carbonyls on Ru based on the comparison with that of the Ru–CO (2016, 2079, and 1951 cm^{-1}) in $[\text{Ru}(\text{CO})_2(\text{PPh}_3)(\mu\text{-SPh})_2]_2$.²⁶ The third absorption peak at 1887 cm^{-1} is assigned to the $\nu(\text{C}\equiv\text{O})$ band of the carbonyl on W based on the comparison with that of the W–CO (1881 cm^{-1}) in $\text{Cp}(\text{CO})\text{-}(\text{Cl})\text{W}(\mu\text{-CMe})(\mu\text{-Cl})\text{Ru}(\text{CO})(\text{PPh}_3)_2$.²⁷ Broad peaks at 1972 and 1887 cm^{-1} may be due to the superposition of the signals of the two isomers in the sample.

In the thermolysis of **1**, one CO on W and the terminal Cl on Ru in **1** are replaced by a terminal Cl and a terminal CO,

respectively, to form **2**, and the environments of the other ligands are kept identical with that of **1** (Figure 2a and b). Ligand migrations in organometallic complexes are common and occur in both intermolecular and intramolecular pathways.^{3–8,28} Isomerization of **1** to **2** is irreversible and is proposed to be intramolecular in nature because the conversion of **1** to **2** is almost quantitative without any byproducts. In addition, thermolysis of **1** under ^{13}C O resulted in the decomposition of **1** before isomerization and no compound **2** was obtained. Complex $\text{CpW}(\text{CO})_3\text{Cl}$ is observed in the decomposition product. This observation further indirectly excludes the intermolecular isomerization process through external CO from W–CO bond breaking to form the Ru–CO bond in **2**. The external CO-induced transfer reaction of a silyl group in the phosphido-bridged bimetallic Fe–Pt system has been observed.²⁸ In addition, bridge/terminal halide exchange and bridge/terminal carbonyl exchange in trinuclear complexes were reported (Chart 1).¹² However, to the best of our knowledge, the internal mutual carbonyl–chloride migration between heteroatoms (W and Ru) in **1** to form **2** has not been observed previously.

In **1**, both chloride and carbonyl ligands have bridging ability. Considering the flexibility of carbonyl and chloride ligands toward terminal/bridging mode, we suggest that the 34e dimer **B** (Scheme 1) is the intermediate during the isomerization of **1** to **2**.

The Ru atom in **1** is electron rich because of the dative W–Ru bonding and the electron-donating phosphine ligand. Donation of an electron from the Ru metal to the π^* of CO on W to form the bridging carbonyl to form the 34e dimer **B** can reduce the electron density on Ru (Scheme 1). The terminal chloride ligand on Ru in **B** can coordinate to the adjacent W to form a bridging chloride and pushes the bridging carbonyl to Ru to accomplish the CO migration. The original bridging chloride ligand completes the chloride migration by converting itself to a W terminal Cl to form **2**. Although we are not able to isolate any intermediate, similar bonding modes of CO and Cl in the proposed intermediate **B** (Scheme 1) were structurally established in $[\text{Rh}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})_2]_2^+$,^{29a} $[\text{Re}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})\text{Cl}_2(\text{EtCN})]_2^+$,^{29b} and $(\text{CO})_3\text{Mo}(\mu\text{-Cl})(\mu\text{-CO})(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{Rh}(\text{NBD})$.^{29c}

The redistribution of electron density in the isomerization of **1** to **2** is revealed by the frequency change of CO absorption peaks in their IR spectra. The lower stretching frequency (1887

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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for **1, **2a**, and **2b****

bonds	1	2a	2b
W1–S1	2.488(2)	2.4720(14)	2.4846(7)
W1–C1	1.993(10)	1.979(7)	1.950(3)
W1–C2	1.999(9)		
W1–C11	2.481(2)	2.4862(15)	2.4734(7)
W1–C12		2.4905(15)	2.4857(8)
W1–C6	2.268(9)	2.253(6)	2.276(3)
W1–C7	2.338(10)	2.291(6)	2.238(3)
W1–C8	2.380(9)	2.381(6)	2.289(3)
W1–C9	2.289(9)	2.363(6)	2.387(4)
W1–C10	2.270(9)	2.285(6)	2.368(3)
Ru1–S1	2.366(2)	2.3921(16)	2.4038(8)
Ru1–C11	2.466(2)	2.4316(15)	2.4514(7)
Ru1–C12	2.401(2)		
Ru1–P1	2.314(2)	2.3847(16)	2.3981(7)
Ru1–C2		1.896(7)	1.905(3)
Ru1–C3	1.818(8)	1.855(7)	1.843(3)
C11–S1	1.793(8)	1.800(6)	1.800(3)
angles			
W1–S1–Ru1	71.54(6)	68.89(4)	68.89(2)
W1–C11–Ru1	70.06(6)	68.05(4)	68.328(19)
S1–W1–C11	73.38(7)	72.65(5)	79.09(2)
S1–W1–C1	82.3(2)	91.24(16)	83.19(2)
S1–W1–C2	130.1(3)		
S1–W1–Ru1	52.22(5)	54.18(4)	54.176(17)
S1–W1–C12		140.39(5)	143.55(3)
C1–W1–C2	76.8(3)		
C1–W1–C11	131.9(2)	131.21(18)	128.25(9)
C1–W1–Ru1	77.5(2)	77.93(17)	74.77(9)
C1–W1–C12		83.77(17)	87.37(9)
C2–W1–C11	88.0(3)		
C2–W1–Ru1	79.0(3)		
C11–W1–Ru1	54.73(5)	55.03(3)	55.460(17)
C11–W1–C12		81.38(5)	79.49(3)
C12–W1–Ru1		86.47(4)	89.38(2)
S1–Ru1–P1	97.86(7)	103.05(5)	109.77(3)
S1–Ru1–C11	75.79(8)	75.02(5)	81.10(3)
S1–Ru1–C12	160.96(8)		
S1–Ru1–C2		161.45(19)	158.26(9)
S1–Ru1–C3	103.0(2)	95.07(18)	89.16(9)
S1–Ru1–W1	56.24(5)	56.93(4)	56.936(18)
P1–Ru1–C11	101.89(8)	98.96(5)	101.60(3)
P1–Ru1–C12	97.17(8)		
P1–Ru1–C2		94.29(19)	91.97(9)

cm^{-1}) of carbonyl on W in **2** than that in **1** (2010 and 1954 cm^{-1}) indicates a stronger back-donation from W to carbonyl in **2**. Consistently, the stretching frequencies of Ru carbonyl ligands in **2** (2033 and 1972 cm^{-1}) are higher than that in **1** (1954 cm^{-1}), indicating a weaker back-donation from Ru to its carbonyl ligands in **2**. This is because the number of π -acceptor carbonyl ligands on the Ru center and W center has been changed from one in **1** to two in **2** and from two in **1** to one in **2**, respectively.

Scrambling of Cl and CO between different metals was reported in the synthesis of $\text{Cp}(\text{CO})(\text{Cl})\text{W}(\mu\text{-CMe})(\mu\text{-Cl})\text{Ru}(\text{CO})(\text{PPh}_3)_2$ by the reaction between $\text{CpW}(\text{CO})_2\text{CMe}$ and $\text{RuCl}_2(\text{PPh}_3)_3$. Chloride and carbonyl migrations between W and Ru were proposed in the reaction; however no intermediate was observed.²⁷ The synthesis of **1** and the conversion of **1** to **2** in this report provide a stepwise and almost quantitative reaction path of the migration of carbonyl ligands from the W to Ru site and chloride ligand from the Ru to W site in the formation of **2** from $\text{CpW}(\text{CO})_3\text{SPh}$ and $\text{RuCl}_2(\text{PPh}_3)_x$ ($x = 3$ and 4).

X-ray Structures of **1, **2a**, and **2b**.** The structures of compounds **1**, **2a**, and **2b** were determined by X-ray diffraction analysis. The ORTEP drawings of **1**, **2a**, and **2b** are shown in Figures 1b, 2a, and 2b, respectively. Selected bond distances and bond angles are listed in Table 1.

These complexes have a similar core structure: one chloride bridge, one thiolato bridge, and a metal–metal bond between the metals. The W1–Ru1 bond distances in **1**, **2a**, and **2b** are 2.8394(9), 2.7481(av), and 2.7657(3) Å, respectively, and are well in accord with the literature values.³⁰ These bond distances are varied according to the variation of their respective acute angles W–S–Ru (71.54(6)°, 68.64 (av)°, and 68.89(2)°) and W–Cl–Ru (70.06(6)°, 68.06(av)°, and 68.328 (19)°). The W1–Ru1 distance (2.8394(9) Å) is comparatively long and is consistent with the dative bonding character. The W1–Ru1 bond distances in **2a** and **2b** are 0.1 Å shorter than that in **1**, implying that metal–metal bonds in **2a** and **2b** are comparatively covalent.

The Cl(1)–W(1)–Ru(1)–S(1) dihedral angles are 96.03(9)°, 93.21(6)°, and 102.33(3)° in **1**, **2a**, and **2b**, respectively. A bigger dihedral angle in **2b** than in **2a** reflects a larger steric hindrance between the phenyl group on the bridging sulfur atom and the bridging chloride. In **2b**, the phenyl group points to the center of the SWRuCl core. In **2a**, the phenyl group points in the opposition direction and has a smaller interaction with the bridging chloride. The SWRuCl core structures of **1** and **2a** are similar, with the phenyl group on the sulfur pointing away from the center of the core.

The average bond distances of Ru1–P1 (2.3914 Å) and Ru–C (1.8747 Å) in **2** are longer than that of Ru1–P1 (2.314(2) Å) and Ru1–C3 (1.818(8) Å) in **1**. This implies that back-donation of electrons from Ru to these ligands is reduced in **2**. This is consistent with the IR data observed.

Conclusions

This paper describes the synthesis of single thiolato-bridged heterodinuclear W–Ru complexes **1** and **2** in high yield. During thermolysis of **1** in toluene, isomerization of **1** to **2** occurred via chloride and carbonyl ligand migration. The migration of the carbonyl and chloride ligands in the conversion of $\text{CpW}(\text{CO})_3\text{SPh} + \text{RuCl}_2(\text{PPh}_3)_x$ ($x = 3$ and 4) \rightarrow **1** \rightarrow **2** is stepwise. Heterobimetallic complexes with early and late transition metals are effective as Lewis acid and Lewis base pairs in catalytic reactions.³¹ Isomerization of **1** to **2** indicates a possibility that the Lewis acidity and Lewis basicity of the metals can be altered by the mutual redistribution of the π -acceptor and σ -donor ligands among the metals during their reactions.

Experimental Section

General Procedures. All reactions and other manipulations were performed under an atmosphere of nitrogen using standard Schlenk

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Table 2. Summary of Crystal Data for **1**, **2a**, and **2b**

	1	2a	2b
formula	C ₃₂ H ₂₅ O ₃ Cl ₂ PSWRu	C ₁₂₉ H ₁₀₀ O ₁₂ Cl ₁₀ P ₄ S ₄ W ₄ Ru ₄	C ₃₂ H ₂₅ O ₃ Cl ₂ PSWRu
fw	876.37	3588.39	876.37
space group	P21/c	P21/c	P $\bar{1}$
a [Å]	10.634(18)	23.134(7)	10.3393(4)
b [Å]	19.703(4)	14.8948(4)	10.4859(4)
c [Å]	14.856(3)	18.7904(5)	16.1041(9)
α [deg]			93.722(2)
β [deg]	103.46(3)	103.8290(10)	101.160(2)
γ [deg]			115.6210(10)
V [Å ³]	3027.2(10)	6287.1(3)	1522.56(12)
ρ (calcd) [Mg m ⁻³]	1.923	1.896	1.912
Z	4	2	2
cryst dimens [mm]	0.31 × 0.16 × 0.13	0.16 × 0.14 × 0.14	0.15 × 0.1 × 0.07
temp [K]	293(2)	293(2)	296(2)
λ (Mo K α) [Å]	0.71073	0.71073	0.71073
2 θ range [deg]	50.0	50.0	50.0
scan type	ω	ω	ω
no. of reflns	5618	41 281	22 333
no. of obsd reflns	5314 (>2.0 σ (I))	11 098 (>2.5 σ (I))	6918 (>2.5 σ (I))
no. of params refined	365	757	370
R	0.0369	0.0362	0.0232
R _w	0.0884	0.0747	0.0513
GoF	0.981	1.062	0.986
D _{map} min., max. [e/Å ³]	-1.631, 1.326	-1.340, 1.340	-0.376, 1.045

techniques. Commercially available chemicals were purchased and used without further purification. All solvents were dried with Na and benzophenone under N₂ and distilled immediately prior to use. Compounds CpW(CO)₃SPh and RuCl₂(PPh₃)_x (x = 3 and 4) were prepared following reported procedures.³² The ¹H and ³¹P{¹H} NMR spectra were recorded using a Bruker Ac-300 spectrometer. Variable-temperature ¹H and ³¹P{¹H} NMR spectra were recorded using a Bruker DRX500/AV400 spectrometer. The ³¹P{¹H} shifts are referenced to 85% H₃PO₄. Microanalyses were performed by use of a Perkin-Elmer 2400 CHN analyzer.

Synthesis of 1. Dichloromethane (50 mL) was added to a solid mixture of CpW(CO)₃SPh (100 mg, 0.226 mmol) and RuCl₂(PPh₃)₃ (216 mg, 0.226 mmol), and the solution was stirred for 12 h at room temperature. The solution was concentrated, and a brown precipitate was obtained by adding hexane. After separation by filtration, the residue was dissolved in dichloromethane (5 mL) and was chromatographed on silica gel using dichloromethane as an eluent. Compound **1** was obtained as a violet solid from the violet band after removing the solvent. Yield: 184 mg, 93%. Anal. Calcd for C₃₂H₂₅O₃PSCl₂WRu: C, 43.82; H, 2.85. Found: C, 43.52, H, 3.11. IR (CH₂Cl₂): ν (CO) 2009 (s), 1954 (vs, br) cm⁻¹. ¹H NMR (CDCl₃): δ 7.73–6.78 (m, 20H, C₆H₅), 5.69 (s, 5H, C₅H₅). ³¹P{¹H} NMR (CH₂Cl₂): δ 57.87 (s). Reaction between CpW(CO)₃SPh (50 mg, 0.113 mmol) and RuCl₂(PPh₃)₄ (138 mg, 0.113 mmol) in dichloromethane (30 mL) under similar reaction conditions afforded **1** in 91% yield (89 mg).

Thermolysis of 1. A toluene solution (30 mL) of **1** (100 mg, 0.114 mmol) was heated at 80 °C for 3 h. The color of the solution changed from violet to yellow. The solvent was removed, and the residue was dissolved in dichloromethane (5 mL). After chromatography on silica gel using dichloromethane/hexane (4:1) as the eluent, compound **2** was obtained with 96% yields (96 mg). Anal. Calcd for C₃₂H₂₅O₃PSCl₂WRu: C, 43.82; H, 2.85. Found: C, 43.49, H, 3.25. IR (CH₂Cl₂): ν (CO) 2033 (vs), 1972 (vs, br), 1887 (m, br) cm⁻¹. ¹H NMR (CDCl₃): δ 7.47–6.78 (m, 20H, C₆H₅), 5.49 (s, 5H, C₅H₅), 5.44 (s, 5H, C₅H₅). ³¹P{¹H} NMR (CH₂Cl₂): δ 46.45 (s), 44.55 (s).

Thermolysis of 1 in the Presence of ¹³CO. A toluene solution (10 mL) of **1** (50 mg, 0.057 mmol) was degassed by freeze–thaw method and was heated at 80 °C for 3 h under ¹³CO. The reaction

mixture was monitored by ³¹P{¹H} and ¹H NMR. Compound **1** was decomposed to CpW(CO)₃Cl³³ with trace amounts of other compounds. No isomerization of **1** to **2** was observed.

Crystal Structure Determination of 1, 2a, and 2b. Single crystals of **1** for X-ray diffraction analysis were grown by slow evaporation of dichloromethane solution layered by hexane at -4 °C. Single crystals of **2a** and **2b** were grown from two sets of crystal growth experiments by ether diffusion into a dichloromethane solution of **2** at -4 and -15 °C, respectively, from the same batch of **2**. The crystals of **1**, **2a**, and **2b** were mounted on a glass fiber for data collection, and the data of **1**, **2a**, and **2b** were collected by using Mo K α radiation at CCD. Detailed data collection parameters are given in Table 2. Data collections were carried out by Mo K α radiation (λ = 0.71073 Å) on a Bruker X8 Apex CCD at room temperature. The unit-cell parameters were obtained by least-squares fit to the automatically centered settings for reflections on a Bruker X8 Apex CCD diffractometer. Intensity data were collected by using the $\omega/2\theta$ scan mode. The structures were solved by direct methods (SHELX-97). All non-hydrogen atoms were located from the difference Fourier maps and were refined by full-matrix least-squares procedures. Hydrogen atoms were included in idealized positions but not refined. Calculations and full-matrix least-squares refinements were performed utilizing the WINGX program package.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond distances and angles; experimental details of the X-ray studies for **1**, **2a**, and **2b**; variable-temperature spectra of ³¹P{¹H} and ¹H NMR. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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