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Mapping the Transformation $[\{Ru^{II}(CO)_3Cl_2\}_2] \rightarrow [Ru^{I}_2(CO)_4]^{2+}$: Implications in Binuclear Water–Gas Shift Chemistry

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Dedicated to Professor Richard A. Walton

Abstract: The complete sequence of reactions in the base-promoted reduction of $[\{Ru^{II}(CO)_3Cl_2\}_2]$ to $[Ru^{I}_2(CO)_4]^{2+}$ has been unraveled. Several μ-OH, μ:κ^2-CO_2H-bridged diruthenium(II) complexes have been synthesized; they are the direct results of the nucleophilic activation of metal-coordinated carbonyls by hydroxides. The isolated compounds are $[Ru_2(CO)_4(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H)_2(\mu\text{-}OH)(NP^F\text{-}Am)_2][PF_6]$ (**1**; NP^F-Am = 2-amino-5,7-trifluoromethyl-1,8-naphthyridine) and $[Ru_2(CO)_4(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H)(\mu\text{-}OH)(NP\text{-}Me_2)_2][BF_4]_2$ (**2**), secured by the applications of naphthyridine derivatives. In the absence of any capping ligand, a tetranuclear complex $[Ru_4(CO)_8(H_2O)_2(\mu^3\text{-}OH)_2(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H)_4][CF_3SO_3]_2$ (**3**) is isolated. The bridging hydroxido ligand in **1** is readily replaced by a π-donor chlorido ligand, which results in $[Ru_2(CO)_4(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H)_2(\mu\text{-}Cl)(NP\text{-}PhOMe)_2][BF_4]$ (**4**). The production of $[Ru_2(CO)_4]^{2+}$ has been attributed to the thermally induced decarboxylation of a bis(hydroxycarbonyl)–diruthenium(II) complex to a dihydrido–diruthenium(II) species, followed by dinuclear reductive elimination of molecular hydrogen with the concomitant formation of the Ru^I–Ru^I single bond. This work was originally instituted to find a reliable synthetic protocol for the $[Ru_2(CO)_4(CH_3CN)_6]^{2+}$ precursor. It is herein prescribed that at least four equivalents of base, complete removal of chlorido ligands by Tl^I salts, and heating at reflux in acetonitrile for a period of four hours are the conditions for the optimal conversion. Premature quenching of the reaction resulted in the isolation of a trinuclear $Ru^I_2Ru^{II}$ complex $[\{Ru(NP\text{-}Am)_2(CO)\}\{Ru_2(NP\text{-}Am)_2(CO)_2(\mu\text{-}CO)_2\}(\mu_3{:}\kappa^3\text{-}C,O,O'\text{-}CO_2)][BF_4]_2$ (**6**). These unprecedented diruthenium compounds are the dinuclear congeners of the water–gas shift (WGS) intermediates. The possibility of a dinuclear pathway eliminates the inherent contradiction of pH demands in the WGS catalytic cycle in an alkaline medium. A cooperative binuclear elimination could be a viable route for hydrogen production in WGS chemistry.

Keywords: carbonyl ligands · hydroxides · organometallics · reaction mechanisms · ruthenium

Introduction

The application of bimetallic systems in homogeneous catalysis is based on the premise that enhanced reaction rate, better selectivity, and new types of reactions might emerge from the cooperation or successive participation of two metal components.[1] Dirhodium complexes are evidently the most effective, with wide-ranging applications in catalytic organic transformations,[2] hydroformylation,[3] and hydrogenation chemistry.[4] Other dimetal systems have shown promise in terms of their activity and/or selectivity.[5] In our continuing effort to advance the landscape of dimetal chemistry, we have explored the chemistry of metal–metal singly bonded diruthenium(I) complex $[Ru_2(CO)_4(CH_3CN)_6][X]_2$ (X = counteranion).[6] Numerous bridged and unsupported diruthenium(I) complexes have been accessed by replacing substitutionally labile acetonitrile ligands with appropriate ligands.[6,7] We have examined the axial modulation of the metal–metal bond in paddlewheel diruthenium(I)

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complexes,[8] performed C–H bond activation,[9] and C–C bond-formation chemistry[10] at the axial site of the $[Ru_2(CO)_4]^{2+}$ core. In 1993, Klemperer et al. reported the synthetic protocol of $[Ru_2(CO)_4(CH_3CN)_6][PF_6]_2$ from the dinuclear precursor $[\{Ru(CO)_3Cl_2\}_2]$ reproduced in Scheme 1.[11] Prompted by our interest in the cooperative bimetallic reactivity, we initiated a program to investigate the base-promoted reduction $[\{Ru^{II}(CO)_3Cl_2\}_2] \rightarrow [Ru^{I}_2(CO)_4]^{2+}$.

$$[Ru(CO)_3Cl_2]_2 + 2NaOH + 4TlPF_6 + 6CH_3CN \rightarrow$$
$$[Ru_2(CO)_4(CH_3CN)_6](PF_6)_2 + CO + CO_2 + H_2O + 2NaPF_6 + 4TlCl$$

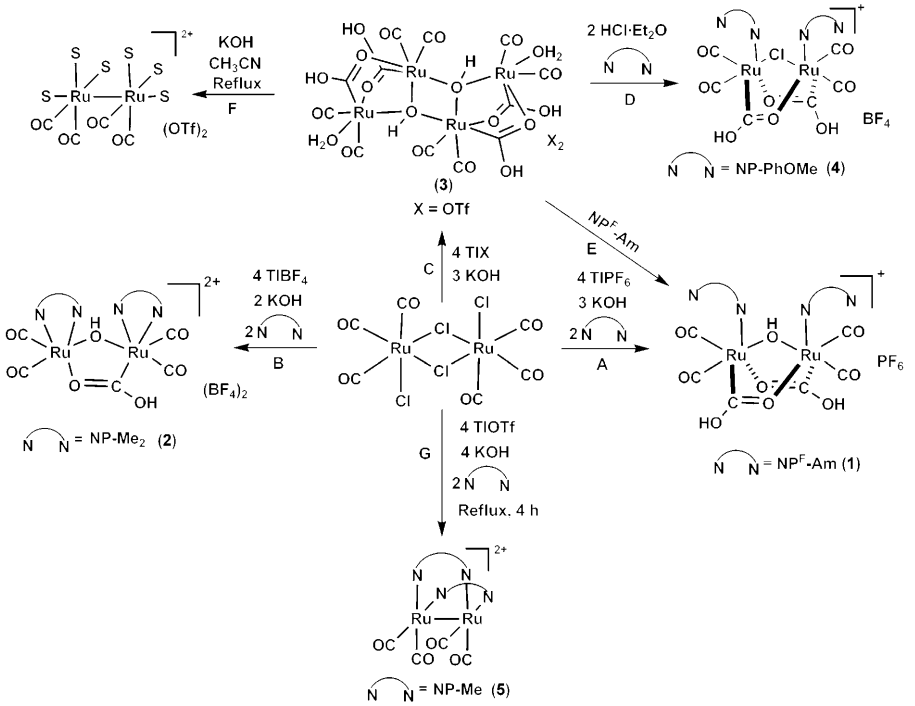
Scheme 1. The synthetic protocol of $[Ru_2(CO)_4(CH_3CN)_6][PF_6]_2$ as reported by Klemperer et al.[11]

Lavigne and co-workers described the reduction of Ru^{II} to Ru^0, which involves the reaction of mononuclear $[Ru(CO)_3Cl_2(thf)]$ with KOH, thus resulting in a hydroxycarbonyl species $[RuCl_2(CO)_2\{C(O)OH\}]^-$, followed by thermally induced decarboxylation under a CO atmosphere to produce $[Ru_3(CO)_{12}]$.[12] The latter reaction is understood in terms of a reductive elimination of HCl from an unstable hydride intermediate "$[RuCl_2(H)(CO)_2]^-$". We suspected that parallel reduction chemistry is effective in Scheme 1, albeit on a diruthenium platform. Reductive elimination on a mononuclear system causes the formal metal oxidation number to decrease by two units, whereas the reduction in valency on a dinuclear system is shared by metals. Therefore, a dinuclear elimination could be a possibility for the conversion of $[Ru^{II}\cdots Ru^{II}]$ to $[Ru^{I}–Ru^{I}]$. In our steps towards unraveling the transformation $[\{Ru(CO)_3Cl_2\}_2] \rightarrow [Ru_2(CO)_4(CH_3CN)_6]^{2+}$, several μ-hydroxido, μ:κ^2-*C*,*O*-hydroxycarbonyl-bridged diruthenium complexes have been isolated. Such complexes are hitherto unknown, and have implications in multinuclear water–gas shift (WGS) chemistry. This work provides mechanistic insight into Klemperer's reaction,[11] and suggests a dinuclear pathway for WGS catalytic cycle.

Results and Discussion

Diruthenium(II) complexes with μ-OH, μ:κ^2-*C*,*O*-CO_2H bridges: The syntheses of these compounds are schematically represented in Scheme 2.

Room-temperature treatment of $[\{Ru(CO)_3Cl_2\}_2]$ with three equivalents of ethanolic KOH in acetonitrile, followed by the addition of $TlPF_6$ to remove chlorido ligands and subsequent addition of 2-amino-5,7-trifluoromethyl-1,8-naphthyridine (NP^F-Am) resulted in a diruthenium(II) complex $[Ru_2(CO)_4(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H)_2(\mu\text{-}OH)(NP^F\text{-}Am)_2][PF_6]$ (**1**) (Scheme 2A). X-ray structural analysis reveals that the cationic unit of **1** consists of two $[Ru(CO)_2(NP^F\text{-}Am)]$ units held together by one μ-hydroxido and two μ:κ^2-*C*,*O*-CO_2H bridges that form a symmetric dinuclear structure (Figure 1). Important bond parameters for compounds **1**–**4** are compared in Table 1. The geometry around each ruthenium atom is approximately octahedral. The Ru–Ru distance (3.4077(3) Å) is rather long for a formal metal–metal bonding interaction, which is in accordance with the total electron count.[13] The bond lengths between the bridging hydroxido oxygen atom and the two ruthenium atoms (Ru1–O1 = 2.138(3), Ru2–O1 = 2.127(3) Å) and Ru1-O1-Ru2 angle (106.04(12)°) fall within the range of normal hydroxido-bridged diruthenium complexes.[14] Two bridged hydroxycarbonyl groups give rise to two four-membered Ru-O-C-Ru rings. The Ru–C and Ru–O bond lengths are as



Scheme 2. The syntheses of compounds **1**–**5** and $[Ru_2(CO)_4(CH_3CN)_6][OTf]_2$. The notation in bold below each arrowhead is used to refer to an individual transformation.

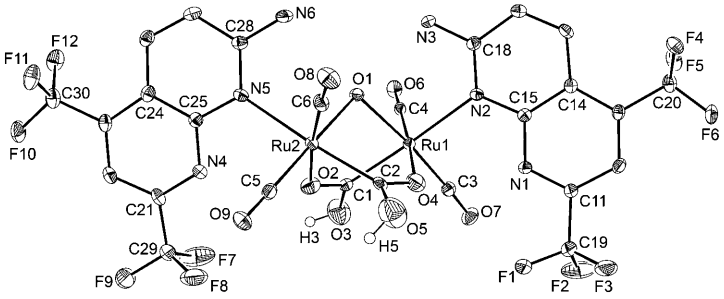


Figure 1. ORTEP diagram (50% probability thermal ellipsoids) of the cationic unit in **1**.

follows: Ru1–C1 = 2.040(4), Ru2–C2 = 2.040(4) and Ru1–O4 = 2.085(3), Ru2–O4 = 2.100(3) Å. Each –C(O)OH bridge has a short C=O bond (C1–O2 = 1.295(5), C2–O4 = 1.288(5) Å) and a long C–O(H) bond (C1–O3 = 1.510(6), C2–O5 = 1.522(6) Å), thus confirming the hydroxycarbonyl bridge.

Each naphthyridine ligand binds to the ruthenium center in monodentate fashion through the N1 atom. The σ-donor carboxyl group exerts a strong *trans* effect, thus resulting in a longer Ru–N bond length. The ^{1}H NMR spectrum of **1** shows one set of signals for naphthyridine protons, which confirms that the two ruthenium centers are in an identical coordination environment in solution. The characteristic IR stretching at 1523 cm^{-1} is attributed to the bridging hydroxycarbonyl group.[15] Bands appearing at 2047 and 1984 cm^{-1} are assigned to C≡O stretching vibrations[16] and a broad band at 3455 cm^{-1} arises due to bridging hydroxido groups.

By following a procedure similar to the synthesis of **1**, the precise addition of two equivalents of base for each molecule of $[\{Ru(CO)_3Cl_2\}_2]$, followed by the removal of chlorido ligands, and subsequent addition of 2,7-dimethyl-1,8-naphthyridine (NP-Me$_2$) resulted in the compound $[Ru_2(CO)_4(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H)(\mu\text{-}OH)(NP\text{-}Me_2)_2][BF_4]_2$ (**2**) (Scheme 2B). The central structure of complex **2** is similar to **1** except that the diruthenium core is bridged by a single $\mu{:}\kappa^2$-*C*,*O*-CO_2H group, as opposed to two such groups in the latter compound, thereby resulting in an asymmetric dinuclear structure (Figure 2). The Ru–Ru distance 3.5650(4) Å in **2** is longer than in compound **1**, which can be attributed to one hydroxycarbonyl bridge. As a consequence, the Ru-O-Ru bridging angle expands from 106.04(12)° in compound **1** to 119.0(2)° in compound **2** (Table 1). Each naphthyridine ligand chelates a ruthenium center by utilizing the N1 and N8 atoms. Interestingly, the diruthenium(II) core loses a CO in the process (vide infra). The ^{1}H NMR spectrum shows a complex pattern at room temperature that reflects the nonequivalence of the naphthyridine ligands, which is consistent with the asymmetrical hydroxycarbonyl bridge. The spectral pattern also reflects that compound **2** exhibits no fluxional behavior that involves effective inversion of the hydroxycarbonyl group in solution at room temperature. The characteristic IR stretching frequency for the hydroxycarbonyl group appears at 1511 cm^{-1}.

Table 1. Comparison of relevant metrical parameters (bond lengths [Å] and angles [°]) for compounds **1**–**4**.

	1	**2**	**3**	**4**
Ru–Ru	3.4077(3)	3.5650(4)	3.3691(4), 3.3654(4)	3.5419(2)
Ru–O (μ-O)	2.138(3), 2.127(3)	2.081(5), 2.057(5)	2.156(6), 2.136(6), 2.121(6), 2.139 (6), 2.261(5),[b] 2.272(6)[b]	2.4628(12), 2.4559(13)[a]
Ru–C (CO_2H)	2.040(4), 2.040(4)	2.028(8)	2.012(8), 2.013(8), 2.017(8), 2.007(8)	2.044(5), 2.045(5)
Ru–O (CO_2H)	2.100(3), 2.085(3)	2.075(7)	2.109(7), 2.097(7), 2.112(7), 2.108(7)	2.096(4), 2.115(4)
C=O	1.295(5), 1.288(5)	1.278(9)	1.316(11), 1.288(10), 1.302(10), 1.297(10)	1.299(6), 1.302(6)
C–OH	1.510(6), 1.522(6)	1.530(10)	1.496(11), 1.529(11), 1.515(11), 1.493(12)	1.519(7), 1.519(7)
Ru–C (CO)	1.860(4)–1.892(4)	1.868(9)–1.881(9)	1.863(10)–1.908(9)	1.910(5)–1841(5)
C–O (CO)	1.136(5)–1.147(5)	1.111(9)–1.154(9)	1.120(10)–1.143(11)	1.121(6)–1.154(6)
Ru–N	2.276(3)–2.295(4)	2.108(6)–2.236(6)	2.230(6)–2.220(6)[c]	2.231(4)–2.249(4)
Ru-O-Ru	106.04(12)	119.0(2)	103.4(2), 104.4(2), 99.0(2),[b] 128.4(3),[b] 99.8(2),[b] 126.3(3)[b]	92.12 (4)[a]
Ru-C-O	116.9(3), 116.5(3)	120.4(6)	115.3(6), 117.0(6), 115.8(6), 116.7(6)	119.3(4), 119.7(4)
Ru-O-C	124.4(3), 125.4(3)	127.2(5)	123.6(6), 124.7(6), 123.3(5), 124.3(6)	125.8(3), 125.8(4)
O-C-O	118.7(4), 119.7(4)	117.5(7)	118.5(7), 118.7(8), 117.8(8), 118.6(8)	117.2(5), 118.1(4)

[a] Ru–Cl (μ-Cl). [b] Bond lengths and angles between two dimeric units. [c] Ru–O.

A reaction sequence similar to the synthesis of **1**, but in the absence of any capping naphthyridine ligand, leads to the formation of a tetranuclear compound $[Ru_4(CO)_8(H_2O)_2(\mu_3\text{-}OH)_2(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H)_4][CF_3SO_3]_2$ (**3**) (Scheme 2C). X-ray structural analysis of the dicationic unit is displayed in Figure 3. Examination of bond and angle parameters suggests that the molecule is best described as the dimer of $\{Ru_2(CO)_4(H_2O)(OH)(CO_2H)_2\}$ fragments fused at two hydroxido oxygen centers.[17] Each fragment closely resembles the diruthenium core in compound **1** with the exclu-

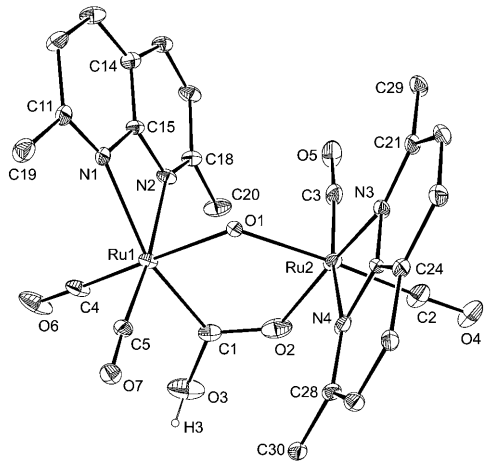


Figure 2. ORTEP diagram (50% probability thermal ellipsoids) of the dicationic unit in **2**.

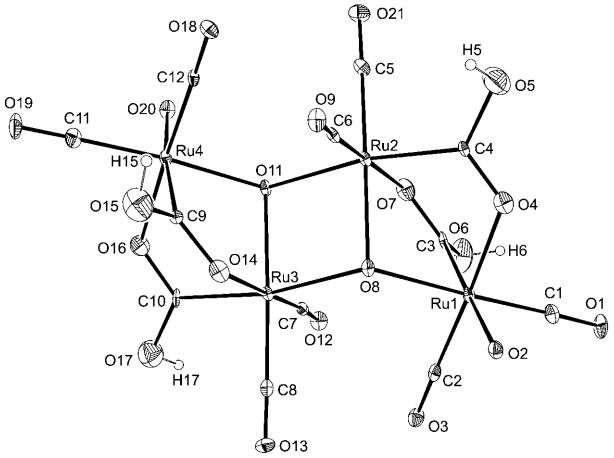


Figure 3. ORTEP diagram (50% probability thermal ellipsoids) of the dicationic unit in **3**.

sion of the naphthyridine ligands. The lack of capping ligands on the metal is fulfilled by the second hydroxido bridge to one ruthenium atom and a water molecule to the other ruthenium in a pair. The Ru–Ru distances are marginally shorter (Ru1–Ru2 = 3.3691(4) and Ru3–Ru4 = 3.3654(4) Å) than the corresponding distance in **1**. The oxygen atom of the μ_3-OH group makes two short bond lengths with a pair of ruthenium atoms and a long bond length with the third ruthenium atom. The short Ru–O bond lengths are in the range 2.121(6)–2.156(6) Å, whereas the long Ru–O bond lengths are 2.272(6) and 2.261(5) Å. The Ru-O-Ru angles range from 99.0(2) to 128.4(3)°. The characteristic IR stretching frequency for the hydroxycarbonyl group appears at 1587 cm^{-1}.

Hydroxycarbonyl-bridged diruthenium complexes are unprecedented in literature.[18] On the contrary, several carbon dioxide[19] and alkoxycarbonyl[20]-bridged complexes have been reported. The dinuclear anion $[Ru_2(CO)_4(\mu\text{-}OCH_3)(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2CH_3)_2Cl_2]$, which bears a structural resemblance to **1**, was obtained by the treatment of $[Ru(CO)_3Cl_3]^-$ with 1.5 equiv of $[CH_3O]^-$ per ruthenium atom.[13c] Two remarkable features that distinguish compounds **1**–**3** are 1) the hydroxycarbonyl bridge between the metal centers, and 2) the ubiquitous presence of the bridging hydroxido ligand. It appears that a π-donor ligand is crucial for the stabilization of the chlorido-free $\{Ru_2(CO)_4(CO_2H)_2\}$ core.

A mechanistic rationalization for the formation of compound **1** involves the initial nucleophilic attack of hydroxides to two coordinated carbonyls in the parent compound $[\{Ru(CO)_3Cl_2\}_2]$. The carbonyl carbon centers are susceptible to nucleophilic attack due to feeble back-donation from Ru^{II}, which leads to instantaneous formation of the bis(hydroxycarbonyl) species. Though the chlorido ligands in the chlorido–ruthenium–carbonyl complex become substitutionally labile upon nucleophilic activation of the carbonyl,[21] we employed equivalent amounts of Tl^I to ensure their complete removal. Subsequently, a hydroxide binds to the diruthenium(II) core, and the incipient vacant coordination site around each Ru center is captured by the naphthyridine ligand.

Exploratory DFT calculations on **1** provide insight on its electronic structure. The carbon atom of the hydroxycarbonyl unit is σ bonded to one Ru and the carbonyl unit is involved in a π interaction with the other Ru.[22] The nature of the bonding changes in going from the π-acceptor CO to σ-donor/weak π-acceptor $\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H$ ligand.[23] Despite the conversion of two carbonyl ligands to hydroxycarbonyl ligands, the loss of four chlorido ligands renders the diruthenium core sufficiently electron deficient, and it readily picks up a hydroxide ion. The remaining coordination vacancies are occupied by two naphthyridine ligands.

To highlight the importance of a π-donor bridge, we set out to synthesize a chloride analogue of **1**. Reaction of two equivalents of an ethereal solution of HCl with $[Ru_4(CO)_8(H_2O)_2(\mu_3\text{-}OH)_2(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H)_4][BF_4]_2$ (the tetrafluoroborate analogue of **3**) and subsequent addition of NP-PhOMe (2-(4-methoxyphenyl)-1,8-naphthyridine) afforded $[Ru_2(CO)_4(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H)_2(\mu\text{-}Cl)(NP\text{-}PhOMe)_2][BF_4]$ (**4**) in high yield (Scheme 2D). This particular combination of the counteranion and the capping ligand was established after several trials that resulted in crystals suitable for X-ray study. The structure of the anionic unit in **4** is shown in Figure 4. The Ru–Ru distance is increased to 3.5419(2) Å (Table 1) to accommodate the bulky chlorido bridging ligand. The Ru-Cl-Ru angle is 92.12(4)°, with the rest of the structural parameters being similar to those of compound **1**.

Controlled use of base leads to the conversion of one carbonyl to hydroxycarbonyl in compound **2**. To maintain the delicate electron balance that results from the loss of four chlorido ligands and the switch of a carbonyl to hydroxycarbonyl, the diruthenium core releases a predominantly π-acceptor carbonyl and accepts a π-donor hydroxido ligand, thus leading to the formation of compound **2**.

In the absence of any capping ligands and in a weakly coordinating solvent, intermolecular association of $\{Ru_2(CO)_4$-

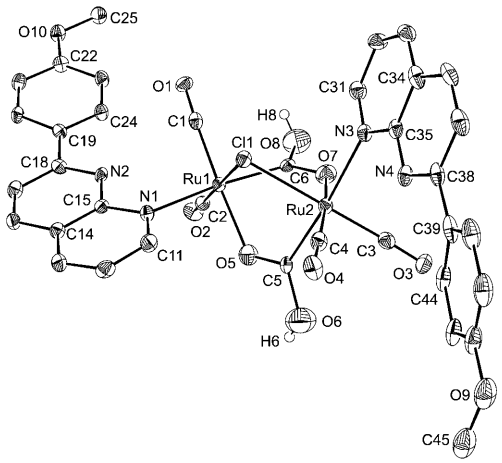


Figure 4. ORTEP diagram (50% probability thermal ellipsoids) of the cationic unit in **4**.

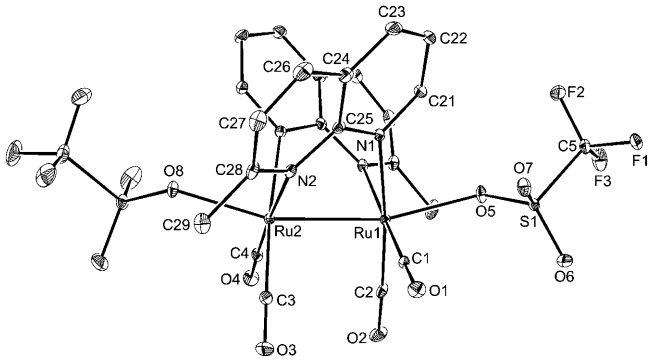


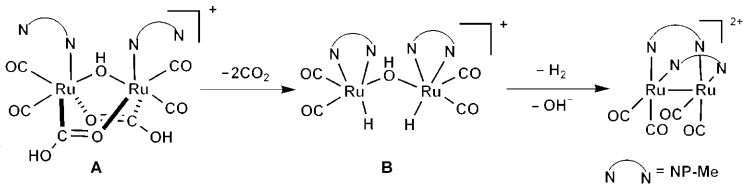
Figure 5. ORTEP diagram (50% probability thermal ellipsoids) of **5** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Important bond parameters [Å]: Ru2–Ru1 2.5995(5), Ru1–N1 2.179(3), Ru1–N4 2.195(3), Ru2–N2 2.203(3), Ru2–N3 2.188(3), Ru1–O5 2.284(3), Ru2–O8 2.240(3); angles [°]: N3-Ru2-N2 86.48(12), N1-Ru1-N4 86.43(12), C3-Ru2-N3 174.88(16), C4-Ru2-N2 176.77(15), C2-Ru1-N1 173.06(16), C1-Ru1-N4 174.45(15); dihedral angles [°]: N3-Ru2-Ru1-N4 −30.79(12), N2-Ru2-Ru1-N1 −30.86(12), C1-Ru1-Ru2-C3 −38.08(18), C2-Ru1-Ru2-C4 −34.97(19).

$(CO_2H)_2(OH)$} units provides compound **3**. When reacted with two equivalents of Am-NP^F, the hexafluorophosphate analogue of **3** quantitatively converts to **1** (Scheme 2E), thus suggesting the hierarchical formation of the tetranuclear complex from its dinuclear congener.

Proposed pathway for the transformation $[\{Ru(CO)_3Cl_2\}_2]$→ $[Ru^I_2(CO)_4]^{2+}$: Isolation and structural characterization of compounds **1**–**4** indicate that the hydroxycarbonyl-bridged diruthenium(II) compounds are potential intermediates in the transformation of $[\{Ru(CO)_3Cl_2\}_2]$ to $[Ru_2(CO)_4]^{2+}$. Indeed, compound **3** readily converts to $[Ru_2(CO)_4(CH_3CN)_6][CF_3SO_3]_2$ in the presence of ethanolic KOH heated at reflux in acetonitrile (Scheme 2F). It should be noted here that the dicationic species $[Ru_2(CO)_4(CH_3CN)_6]^{2+}$ has not been structurally characterized; however, applications of various ligands have led to numerous complexes containing the $[Ru_2(CO)_4]^{2+}$ core.[6–11] We have employed naphthyridine derivatives to bridge the singly bonded Ru^I–Ru^I core, thus giving additional support to the metal–metal bond.[6,7b,8–10]

A single-pot reaction that contains $[\{Ru(CO)_3Cl_2\}_2]$, four equivalents of KOH, four equivalents of $TlCF_3SO_3$, and two equivalents of 2-methyl-1,8-naphthyridine (NP-Me) in acetonitrile heated at reflux for 4 h afforded $[Ru_2(CO)_4(NP\text{-}Me)_2(CF_3SO_3)_2]$ (**5**) (Scheme 2G).[10,24] The structure of **5** is shown in Figure 5; bond parameters are given in the corresponding caption.

A reaction course is proposed that involves the nucleophilic activation of carbonyls, followed by decarboxylation, and subsequent binuclear reductive elimination of molecular hydrogen, thus leading to the formation of a $\{Ru^I_2(CO)_4\}^{2+}$ core. The intermediate **A**, an NP-Me analogue of **1**, is formed initially that undergoes a thermally induced decarboxylation process to provide dihydrido(μ-hydroxido)diruthenium(II) intermediate **B** (Scheme 3).[25] Several mixed hydrido–hydroxido complexes are structurally characterized, most of which involve third-row transition metals.[26] A few



Scheme 3. Proposed reaction course for the formation of the $\{Ru^I_2(CO)_4\}^{2+}$ core involving decarboxylation followed by dinuclear reductive elimination of molecular hydrogen.

ruthenium clusters supported by hydrido and hydroxido ligands have been reported.[27] Onishi's $[\{Ru(CO)(PMe_3)_2\}_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{:}\kappa^2\text{-}C,O\text{-}CO_2)]$ is an example of a carbon dioxide bridged diruthenium(II) complex that contains μ-hydrido and μ-hydroxido ligands.[28] Milstein's (μ-hydroxido)–dihydrido–diiridium complexes represent a unique set of diiridium compounds that involve a bridging hydroxido and two terminal hydrido ligands.[26a–c] Despite our best efforts, species **B** could not be characterized. Relatively poor stability of the dihydrido compounds of second-row transition metals serves to rationalize our inability to isolate the dihydride intermediate.[29] A DFT-optimized structure of **B**, however, was obtained; it is shown in Figure 6. Harmonic frequency calculations confirm the structure to be an energy minimum. The intermediate **B** consists of a hydroxido-bridged diruthenium core. Each ruthenium is additionally coordinated to one chelating naphthyridine, two carbonyl ligands, and a terminal hydrido ligand. The calculated Ru–Ru distance is 3.8286 Å, the Ru–H bond lengths are 1.5685 and 1.5679 Å, and the Ru-O-Ru angle is 126.53°. Two hydrido ligands are in a staggered disposition reflected in the H-Ru-Ru-H dihedral angle of 54°. It is our assertion that the dihydride species **B** undergoes cooperative dinuclear reductive elimination, which evolves molecular hydrogen, with simultaneous release of the hydroxide and concomitant formation of the

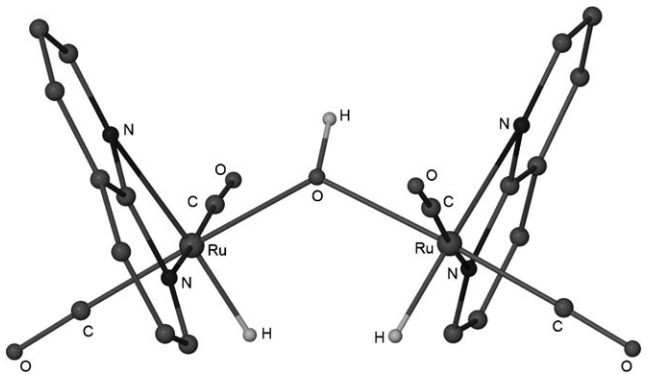


Figure 6. DFT-optimized structure of **B**.

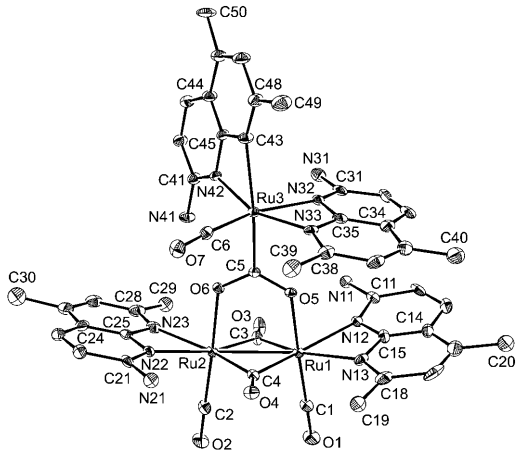


Figure 7. ORTEP diagram (50% probability thermal ellipsoids) of the dicationic unit in **6** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Important bond parameters [Å]: Ru1–Ru2 2.6712(9), Ru1–O5 2.090(4), Ru2–O6 2.098(4), C5–O5 1.273(8), C5–O6 1.297(8), Ru3–C5 2.014(6), Ru1–C3 2.008(7), Ru2–C3 2.004(7), Ru1–C4 1.986(7), Ru2–C4 1.996(8), Ru1–N12 2.255(6), Ru1–N13 2.195(6), Ru2–N22 2.221(6), Ru2–N23 2.222(7), Ru3–N33 2.072(6), Ru3–N42 2.108(6), Ru3–N32 2.193(6), Ru3–N43 2.250(6), Ru1–C1 1.858(8), Ru2–C2 1.875(8), Ru3–C6 1.830(8), O4–C4 1.191(9), O3–C3 1.163(8), O1–C1 1.146(9), O2–C2 1.124(9), O7–C6 1.138(9); angles [°]: O5-C5-O6 21.9(6), Ru2-C3-Ru1 83.5(3), Ru1-C4-Ru2 84.3(3), C5-O5-Ru1 125.3(4), C5-O6-Ru2 123.4(4).

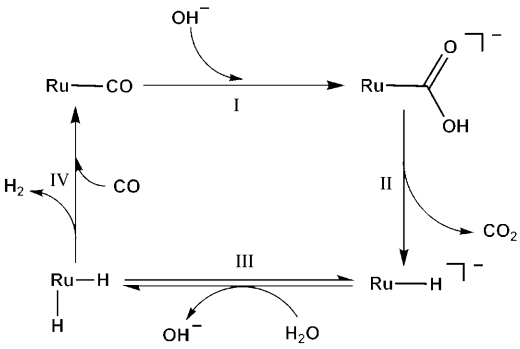
Ru^{I}–Ru^{I} single bond.[25c] The naphthyridine changes its coordination from a chelating to bridging mode, thereby spanning the dimetal core in forming $[Ru_2(CO)_4(NP\text{-}Me)_2(CF_3SO_3)_2]$ (**5**).

The detection of hydrogen as one of the side products in this transformation provides additional support in favor of this mechanism. GC analysis of the gaseous products obtained in a sealed-tube experiment revealed molecular hydrogen.[30] It is in contrast to Klemperer's Scheme (Scheme 1) in which CO_2 and H_2O are purported to be the side products. The unambiguous detection of hydrogen gives credence to the proposed dinuclear pathway for this transformation.

Premature quenching and isolation of the 'CO_2'-bridged species: In our quest to identify the dihydride intermediate of type **B** (Scheme 3), the reaction was quenched prematurely and the products were analyzed. Although we failed to characterize a metal hydride species from NMR spectroscopy analyses, a yellow solid was isolated by employing 2-amino-5,7-dimethyl-1,8-naphthyridine (NP-Am). X-ray analysis disclosed the formulation of a trinuclear cluster $[\{Ru(NP\text{-}Am)_2(CO)\}\{Ru_2(NP\text{-}Am)_2(CO)_2(\mu\text{-}CO)_2\}(\mu_3{:}\kappa^3\text{-}C,O,O'\text{-}CO_2)][BF_4]_2$ (**6**). The triruthenium ensemble consists of a metal–metal singly bonded diruthenium $[Ru^{I}_2(\mu\text{-}CO)_2(CO)_2(NP\text{-}Am)_2]$ core and a mononuclear $\{Ru^{II}(NP\ Am)_2(CO)\}$ unit bridged by $\mu_3{:}\kappa^3\text{-}C,O,O'\text{-}CO_2$ (Figure 7). The oxygen atoms bridge the diruthenium core and the carbon atom is bonded to the third ruthenium. The Ru1–Ru2 distance of 2.6712(9) Å confirms the single bond between the metal atoms.[6–10] A small difference between C5–O5 (1.272(8) Å) and C5–O6 (1.297(8) Å) bond lengths in the CO_2 unit suggests delocalization within the fragment.[31] The Ru3–C5 bond length is 2.015(7) Å. The $\{Ru_2(NP\text{-}Am)_2(CO)_2\}$ unit adopts an edge-sharing bioctahedral (ESBO) configuration with each ruthenium atom coordinated to a chelating naphthyridine, two bridging CO, one terminal CO, and an oxygen atom from the CO_2 fragment. The Ru atom in the mononuclear unit is in a pseudo-octahedral environment coordinated to two *cis*-NP ligands. Only a handful of trinuclear complexes supported by a $\mu_3{:}\kappa^3\text{-}CO_2^{2-}$ bridge are known;[32] however, similar chemistry with ruthenium is unprecedented.

Complex **6** is the result of an incomplete decarboxylation process. The singly bonded $\{Ru^{I}_2(\mu\text{-}CO)_2(CO)_2(NP\text{-}Am)_2\}$ unit reflects the dinuclear reduction, whereas the mononuclear $\{(Ru^{II}(NP\text{-}Am)_2(CO)(CO_2)\}$ is indicative of incomplete decarboxylation.

Implications in water–gas shift (WGS) chemistry: Homogeneous catalysis of the WGS reaction by metal carbonyls in alkaline solution has been widely recognized to follow a cycle shown as in Scheme 4.[33] It involves the initial activation of metal-coordinated CO to a hydroxycarbonyl complex $M(CO_2H)^-$, followed by decarboxylation to a metal hydride anion MH^-; protonation of the latter affords a metal dihy-



Scheme 4. Mechanism of the WGS reaction catalyzed by metal carbonyls in alkaline solution.[33]

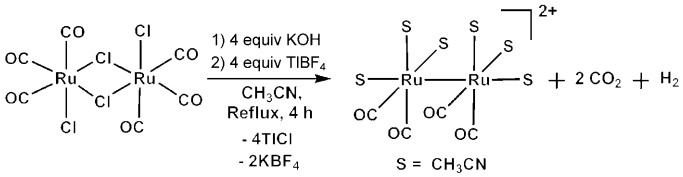
dride, and finally reductive elimination of H_2 and regeneration of the original metal carbonyl by reaction with CO.

The first homogeneous WGS reaction in alkaline solution was based on the use of a trinuclear complex $[Ru_3(CO)_{12}]$.[33a] The general mechanism, however, features a single metal site as the reaction center, although there has been credible evidence in support of the integrity of the trinuclear cluster being intact in solution under the reaction conditions.[34] Our study raises the possibility of a dinuclear pathway. The implication of this possibility in WGS catalysis is significant on two counts. 1) Ford and co-workers indicated the contradictory pH requirements for two important steps in Scheme 4. In step I, the activation of coordinated carbonyl by hydroxide would be favored by increasing the pH. In contrast, the protonation of the $[Ru{-}H]^-$ by water, in step III, would be suppressed at high pH. Based on insight gained in this study, we suggest the intermediacy of dinuclear intermediates in the WGS mechanism. Simultaneous activation of two carbonyls to hydroxycarbonyls on a diruthenium platform, followed by decarboxylation to a dihydrido–diruthenium species would remove the contradictory pH demands. 2) Dinuclear elimination of an organic product has been invoked to rationalize the enhanced rate in homogeneous cluster catalysis.[35] The presence of a second metal causes rate enhancement in hydrogen elimination from a metal hydride that exhibits sluggish intramolecular elimination otherwise.[36] A dinuclear elimination of hydrogen is proven to be the faster process compared to its mononuclear route.[3a–b,35,37] The hydrogen reactivity on a diiridium core has been studied extensively by Nocera and co-workers, thus illustrating the bimetallic cooperativity in hydrogen addition and elimination processes.[38] We propose a binuclear elimination reaction for the hydrogen-production step in WGS chemistry.

Conclusion

In this work we have documented the complete sequence of reactions starting from $[\{Ru(CO)_3Cl_2\}_2]$ to its conversion to $[Ru_2(CO)_4]^{2+}$ core. The base-promoted reduction proceeds by means of nucleophilic activation of carbonyls, thereby resulting in the μ-hydroxido, μ_2:κ^2-hydroxycarbonyl-bridged diruthenium(II) complexes. Isolation and structural characterization of compounds **1**–**4** provides evidence for the intermediacy of such species in this transformation. Thermally induced decarboxylation affords a dihydrido–diruthenium intermediate, which undergoes dinuclear reductive elimination of hydrogen and results in the diruthenium(I) core. The structure of a (μ-hydroxido)–dihydrido–diruthenium(II) species has been optimized at the DFT level of theory, and the eliminated hydrogen gas has been confirmed by GC analysis.

The procedure prescribed by Klemperer et al.[11] provides easy access to the diruthenium(I) precursor complex $[Ru_2(CO)_4(CH_3CN)_6]^{2+}$.[39] It is, however, our observation that use of four equivalents of base and heating at reflux for four hours in acetonitrile provide the identical product with similar yield (80–85 %) and excellent purity.[40] On the basis of our findings, we offer an alternate scheme in which the byproducts are carbon dioxide and hydrogen (Scheme 5).



Scheme 5. An alternative scheme for the synthesis of $\{Ru^{I}_2(CO)_4\}^{2+}$ from $[Ru^{II}(CO)_3Cl_2]$.

The reactions involved in this transformation are reminiscent of WGS chemistry. Our study insinuates a dinuclear mechanism for WGS catalysis. The intermediacy of dinuclear intermediates eliminates the inherent contradiction of pH demands in the catalytic cycle. Further, synergism between two metals is anticipated to enhance the rate of hydrogen elimination. Even for a mononuclear catalyst, the possibility of a di- or multinuclear mechanism may not be ruled out under WGS reaction conditions.[41]

Finally, the role of naphthyridine ligands in this chemistry should not be underrated. A host of naphthyridine derivatives (NP−R) are employed in the successful isolation of diruthenium intermediates. The NP ligand switches its coordination mode from monodentate (η^1) to chelating (η^2) to bridging (μ^2), as illustrated in Scheme 3, to accommodate electronic and structural reorganization of the diruthenium core.[6] Low-energy flexing of naphthyridine modes are important adjuncts, as significant reorganization of the primary coordination environment occurs in the cooperative binuclear elimination process.

Experimental Section

General procedures: All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using a standard Schlenk vessel and vacuum line techniques. ^{1}H NMR spectra were obtained using JEOL JNM-LA 400 and 500 MHz spectrometers. ^{1}H NMR spectroscopic chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. Elemental analyses were performed using a Thermoquest EA1110 CHNS/O analyzer. The crystallized compounds were powdered, washed several times with dry diethyl ether, and dried under vacuum for at least 48 h prior to elemental analyses. ESIMS was recorded using a Waters Micromass Quattro Micro triple-quadrupole mass spectrometer. ESIMS of all complexes was recorded in acetonitrile. The GC experiment was performed using an Agilent 7890A GC system. Infrared spectra were recorded in the range of 4000–400 cm^{-1} using a Vertex 70 Bruker spectrophotometer.

Materials: Solvents were dried by conventional methods, distilled under nitrogen, and deoxygenated prior to use.[42] $RuCl_3{\cdot}xH_2O$ was purchased from Arora Matthey, India. 2-Amino-5,7-bis(trifluoromethyl)-1,8-naphthyridine,[43] 2-(4-methoxyphenyl)-1,8-naphthyridine,[44] 2,7-dimethyl-1,8-naphthyridine,[45] and 2-amino-5,7-dimethyl-1,8-naphthyridine[46] ligands were synthesized and purified according to literature procedures.

Synthesis of metal complexes

Complex ***1***: A 1 M solution of KOH in ethanol (0.3 mL, 0.3 mmol) was added slowly to a suspension of $[\{Ru(CO)_3Cl_2\}_2]$ (50 mg, 0.098 mmol) in acetonitrile. $TlPF_6$ (157 mg, 0.449 mmol) and 2-amino-5,7-bis(trifluoromethyl)-1,8-naphthyridine (64 mg, 0.23 mmol) were subsequently added to the cloudy yellow solution. All reagents were added in a span of five minutes, and the mixture was stirred for one hour at room temperature. The white precipitate was removed by filtration. The bright yellow solution was concentrated and diethyl ether was added to induce a precipitate. The yellow precipitate was washed with diethyl ether (3×10 mL) and dried. The solid material was dissolved in dichloromethane (3 mL) to leave a small amount of white solid, which was removed by filtration. The filtrate was concentrated and diethyl ether was added to it to induce precipitation. Repeated washing followed by prolonged drying under vacuum provided a yellow solid. Crystals suitable for X-ray study were grown by layering petroleum ether over a solution of the compound in dichloromethane. Yield: 70 mg (68%); ^{1}H NMR (CD_2Cl_2): δ=8.20–8.19 (d, 2H), 7.88 (s, 2H), 7.16–7.15 ppm (d, 2H); IR (KBr): $\tilde{\nu}$=2046 (s; ν(CO)), 1986 (s; ν(CO)), 1528 (m; ν(OCO)), 847 cm^{-1} (vs; ν(PF_6)); elemental analysis calcd (%) for $C_{26}H_{13}N_6O_9PF_{18}Ru_2$: C 27.67, H 1.16, N 7.45; found: C 27.81, H 1.03, N, 7.27.

Complex ***2***: Slow addition of a 1 M KOH solution in ethanol (0.2 mL, 0.2 mmol) to $[\{Ru(CO)_3Cl_2\}_2]$ (50 mg, 0.098 mmol), followed by $TlBF_4$ (117 mg, 0.402 mmol) and 2,7-dimethyl-1,8-naphthyridine (32 mg, 0.202 mmol) was carried out in acetonitrile following a similar procedure as described in the synthesis of the complex **1**. Single crystals suitable for X-ray study were grown by layering petroleum ether over a solution of the compound in dichloromethane. Yield: 46 mg (64%); ^{1}H NMR (CD_3CN): δ=8.55–8.51 (m, 2H), 8.48–8.44 (m, 4H), 8.14–8.12 (d, 2H), 7.74–7.67 (m, 5H), 7.59–7.53 (q, 1H), 7.37–7.35 (d, 2H), 2.80–2.61 ppm (multiple singlets; CH_3); IR (KBr): $\tilde{\nu}$=2057 (s; ν(CO)), 2012 (s; ν(CO)), 1962 (s; ν(CO)), 1511 (m; ν(OCO)), 1060 cm^{-1} (s; ν(BF_4)); elemental analysis calcd (%) for $C_{25}H_{22}N_4O_7B_2F_8Ru_2$: C 34.66, H 2.56, N 6.47; found: C 33.98, H 2.11, N 6.71.

Complex ***3***: A 1 M solution of KOH in ethanol (0.3 mL, 0.3 mmol) was added slowly to a suspension of $[\{Ru(CO)_3Cl_2\}_2]$ (50 mg, 0.098 mmol) in acetonitrile. TlOTf (159 mg, 0.449 mmol) was subsequently added to the solution. The mixture was stirred for 1 h at room temperature. The white precipitate was removed by filtration. The bright yellow solution was concentrated and left at low temperature (−4 °C) in a conical flask for crystallization. Crystals were harvested after two weeks, washed with diethyl ether, and dried under vacuum. Yield: 32 mg (42%); IR (KBr): $\tilde{\nu}$= 2030 (s; ν(CO)), 1957 (s; ν(CO)), 1584 (m; ν(OCO)), 1285 cm^{-1} (ν-(OTf)); elemental analysis calcd (%) for $C_{14}H_{10}O_{26}F_6S_2Ru_2$: C 14.29, H 0.86; found: C 13.98, H 0.77.

Complex ***4***: The tetrafluoroborate and hexafluorophosphate analogues of **3** were synthesized by following an identical procedure employing corresponding Tl^I salts, and the products were not characterized further. A 1 M ethereal solution of HCl (0.115 mL, 0.115 mmol) was added slowly to an acetonitrile solution of $[Ru_4(CO)_8(H_2O)_2(\mu_3\text{-}OH)_2(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H)_4][BF_4]_2$ (50 mg, 0.059 mmol) at room temperature. 2-(2-Methoxyphenyl)-1,8-naphthyridine (55 mg, 0.233 mmol) was added to it and the reaction mixture was stirred for 30 min. The resultant yellow solution was concentrated and diethyl ether was added to induce precipitation. Repeated washing by diethyl ether followed by prolonged drying under vacuum provided a yellow solid. Single crystals were grown by layering hexane over a solution of the compound in dichloromethane. Yield: 0.045 (76%); ^{1}H NMR (CD_3CN): δ=9.03 (s, 1H), 8.35–8.33 (d, 1H), 8.3–8.28 (d, 1H), 8.26–8.24 (d, 2H), 8.07–8.06 (d, 1H), 7.5–7.48 (q, 1H), 7.09–7.08 (d, 2H), 3.86 ppm (s, 3H); IR (KBr): $\tilde{\nu}$=2050 (s; ν(CO)), 1980 (s; ν(CO)), 1550 (m; ν(OCO)), 1064 cm^{-1} (s; ν(BF_4)); elemental analysis calcd (%) for $C_{36}H_{26}N_4O_{10}ClBF_4Ru_2$: C 43.28, H 2.62, N 5.61; found: C 43.81, H 2.69, N 5.73.

Complex ***6***: A 1 M solution of KOH in ethanol (0.3 mL, 0.3 mmol) was added slowly to a suspension of $[\{Ru(CO)_3Cl_2\}_2]$ (50 mg, 0.098 mmol) in acetonitrile. $TlBF_4$ (117 mg, 0.402 mmol) and 2-amino-5,7-dimethyl-1,8-naphthyridine (43 mg, 0.247 mmol) were subsequently added to the cloudy yellow solution. The mixture was heated at reflux for 2.5 h. The white precipitate was removed by filtration. The bright yellow solution was concentrated and diethyl ether was added to induce a precipitate. The yellow precipitate was washed with diethyl ether and dried. The solid material was dissolved in dichloromethane (3 mL) to leave a small amount of white solid, which was removed by filtration. The filtrate was concentrated and diethyl ether was added to it to induce precipitation. Repeated washing followed by prolonged drying under vacuum provided a yellow solid. Crystals suitable for X-ray study were grown by layering petroleum ether over a solution of the compound in dichloromethane. Yield: 34 mg (26%); ^{1}H NMR (CD_3CN): δ=8.14 (m, H; NP), 7.86 (m, H; NP), 7.14 (s, H; NP), 7.05 (m, H; NP), 6.79 (m, H; NP), 6.68 (m, H; NP), 2.89–2.77 (multiple singlets; CH_3), 2.66 (s; CH_3), 2.57–2.38 ppm (multiple singlets; CH_3); IR (KBr): $\tilde{\nu}$=2022 (s; ν(CO)), 1954 (s; ν(CO)), 1435 (ν(OCO)), 3360 (br; ν(NH_2)), 1062 cm^{-1} (ν(BF_4^-)); elemental analysis calcd (%) for $C_{46}H_{44}N_{12}O_7B_2F_8Ru_3$: C 40.81, H 3.28, N 12.42; found: C 40.72, H 3.33, N 12.55; MS (ESI): *m*/*z*: 1180 $[M]^+$, 1268 $[M^2{+}{+}BF_4^-]^+$.

Conversion of 3 to 1: 2-Amino-5,7-bis(trifluoromethyl)-1,8-naphthyridine (28 mg, 0.098 mmol) was added to a solution of $[Ru_4(CO)_8(H_2O)_2(\mu_3\text{-}OH)_2(\mu{:}\kappa^2\text{-}C,O\text{-}CO_2H)_4][PF_6]_2$ in acetonitrile (25 mg, 0.024 mmol), the hexafluorophosphate analogue of **3**. The solution was stirred at room temperature for 2 h. The bright yellow solution was concentrated and diethyl ether was added to induce precipitation. Repeated washing followed by crystallization in a dichloromethane/petroleum ether mixture provided **1**. Yield: 20 mg (77%).

Conversion of 3 to $[Ru_2(CO)_4(CH_3CN)_6][CF_3SO_3]_2$: A 1 M solution of KOH in ethanol (0.09 mL, 0.09 mmol) was added slowly to a solution of **3** (50 mg, 0.04 mmol) in acetonitrile and the mixture was heated at reflux for four hours. The solution was allowed to cool to room temperature, $[tBu_4N][CF_3SO_3]$ (34 mg, 0.09 mmol) was added to it and it was stirred for 1 h. The bright orange solution was concentrated and diethyl ether was added to it. The sticky solid was washed with diethyl ether (3×5 mL) and dried under vacuum. It was redissolved in acetonitrile (1 mL), diethyl ether was added slowly to induce precipitation, and the solid was washed several times with diethyl ether and dried under vacuum. This process was repeated three times to obtain an analytically pure compound. Yield: 60 mg (85%); IR (KBr): $\tilde{\nu}$=2034 (s; ν(CO)), 1999 (s; ν(CO)), 1955 (s; ν(CO)), 1264 cm^{-1} (ν(OTf)); elemental analysis calcd (%) for $C_{18}H_{18}N_6S_2O_{10}F_6Ru_2$: C 25.18, H 2.11, N 9.79; found: C 25.12, H 1.97, N 9.83.

X-ray data collection and refinement: Single-crystal X-ray structural studies were performed using a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2) K using graphite-monochromated $Mo_{K\alpha}$ radiation (λ_α=0.71073 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages,[47] and the data were corrected for absorption using the SADABS program.[48] The structures were solved and refined using the SHELX suite of programs,[49] whereas additional crystallographic calculations were performed by the PLATON program.[50] Pertinent details of data collection and final refinement parameters for **1**–**6** are collected in Table 2. Figures were drawn using ORTEP32.[51] CCDC-750482 (**1**), -750483 (**2**), -750484 (**3**), -750485 (**4**), -750486 (**5**), and -750487 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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[1] a) *Multimetallic Catalysis in Organic Synthesis* (Eds.: M. Shibasaki, Y. Yamamoto), Wiley-VCH, Weinheim, **2004**; b) R. A. Adams, F. A.

Table 2. Crystallographic data and pertinent refinement parameters for compounds **1**–**6**.

	1	**2**	**3**	**4·CH_2Cl_2**	**5**	**6·2 CH_2Cl_2**
formula	$C_{26}H_{12}F_{18}N_6O_9PRu_2$	$C_{25}H_{21}B_2C_{10}F_8N_4O_7Ru_2$	$C_{14}H_{10}F_6O_{26}Ru_4S_2$	$C_{37}H_{28}BCl_3F_4N_4O_{10}Ru_2$	$C_{24}H_{16}F_6N_4O_{10}Ru_2S_2$	$C_{48}H_{26}B_2Cl_4F_8N_{12}O_7Ru_3$
M_r	1127.53	865.22	1176.62	1083.93	900.67	1501.44
crystal system	triclinic	triclinic	monoclinic	monoclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	*Pbca*	$P\bar{1}$
a [Å]	10.3288(8)	12.8447(19)	12.6091(17)	16.3864(13)	13.3008(10)	12.0535(12)
b [Å]	12.9180(10)	15.857(2)	15.732(2)	10.1872(8)	14.1949(10)	12.2007(13)
c [Å]	15.5037(12)	19.100(3)	17.996(3)	26.069(2)	33.346(2)	22.495(2)
α [°]	80.5780(10)	76.554(3)	90.00	90.00	90.00	90.526(2)
β [°]	82.3090(10)	75.902(2)	102.849(2)	106.8950(10)	–	99.979(2)
γ [°]	67.9870(10)	87.593(3)	90.00	90.00	–	109.603(2)
V [Å^3]	1886.0(3)	3669.1(9)	3480.4(8)	4163.9(6)	6295.8(8)	3061.2(6)
Z	2	4	4	4	8	2
ρ_{calcd} [g cm^{-3}]	1.985	1.566	2.246	1.729	1.900	1.629
μ [mm^{-1}]	0.990	0.906	1.947	0.996	1.187	0.986
$F(000)$	1094	1700	2256	2152	3536	1472
collected reflns	16840	33324	23643	36564	40180	17507
independent reflns	8938	17604	5929	10202	7822	12161
obsd reflns [$I>2\sigma(I)$]	6896	7216	4617	6813	7134	9093
no. of variables	561	829	501	554	435	734
GOF	1.034	0.850	1.060	1.014	1.232	1.073
R_{int}	0.0330	0.0750	0.0660	0.0693	0.0564	0.0297
final R indices	$R1=0.0476$	$R1=0.0476$	$R1=0.0592$	$R1=0.0590$	$R1=0.0541$	$R1=0.0743$
$[I>2\sigma(I)]$[a]	$wR2=0.1154$	$wR2=0.1154$	$wR2=0.1345$	$wR2=0.1179$	$wR2=0.1109$	$wR2=0.1685$
R indices (all	$R1=0.0653$	$R1=0.0653$	$R1=0.0785$	$R1=0.0978$	$R1=0.0606$	$R1=0.0997$
data)[a]	$wR2=0.1305$	$wR2=0.1305$	$wR2=0.1465$	$wR2=0.1378$	$wR2=0.1139$	$wR2=0.1793$

[a] $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ with $F_o^2>2\sigma(F_o^2)$. $wR2=[\Sigma w(|F_o^2|-|F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$.

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[24] $[\{Ru(CO)_3Cl_2\}_2]$ (55 mg, 0.105 mmol), 1 M ethanolic KOH (0.45 mL, 0.45 mmol), TlOTf (0.155 mg, 0.44 mmol), and 2-methyl-naphthyridine (NP-Me) (32 mg, 0.22 mmol) were added to acetonitrile (10 mL) and the mixture was heated at reflux for 4 h. The white precipitate was removed by filtration. The resulting orange solution was concentrated under vacuum, and diethyl ether (15 mL) was added with stirring to induce precipitation. The solid residue obtained was washed with diethyl ether (3×5 mL) and dried under vacuum. Yield: 49 mg (51%). Compound **5** was obtained in high yield from the reaction of $[Ru_2(CO)_4(MeCN)_6][BF_4]_2$ with 2-MeNP (31 mg, 0.21 mmol) in acetonitrile; see reference [10].

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