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ORGANOMETALLICS
Note

Formation of an Iodide-Bridged Diruthenium Complex from [(η^5-Ph_4C_4COH)$(CO)_2$RuI] and [(Ph_4C_4CO)$(CO)_2Ru]_2$: An Efficient Catalyst for Alcohol Oxidation with Ag_2O

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Summary: Iodide-bridged diruthenium complexes, [(η^5-2,5-R_2-3,4-Ph_2C_4COH)$(CO)_2$Ru−(μ-I)−Ru$(CO)_2$(η^4-2,5-R_2-3,4-Ph_2C_4CO)] *(**6a**, R = Ph;* ***6b**, R = Me), were formed from the reaction of* (η^5-2,5-R_2-3,4-Ph_2C_4COH)$(CO)_2$RuI *(**2c**, R = Ph;* ***2d**, R = Me) with* [(2,5-R_2-3,4-Ph_2C_4CO)$(CO)_2Ru]_2$ *(**7a**, R = Ph;* ***7b**, R = Me). The complexes exhibited a high catalytic activity for the oxidation of alcohols with silver oxide at room temperature.*

Shvo's complex **1** exhibits intriguing catalytic activities for many hydrogen-transfer reactions such as hydrogenation of alkynes,[1,2] reduction of ketones,[3] oxidation of alcohols,[4] Tishchenko-type disproportionation of aldehydes,[5] and oxidant-free dehydrogenation of alcohols.[6] Moreover, it is also an excellent catalyst for the racemization of secondary alcohols under the conditions for the dynamic kinetic resolution (DKR) of alcohols with enzymes and acylating reagents.[7] Recently, Bäckvall and co-workers have reported its activity also for the racemization of amines.[8] However, heating was required to activate **1** dormant under ambient conditions, and it was proposed that heating cleaves **1** into ruthenium hydride complex **2a** and 16-electron ruthenium cyclopentadienone species **3** (Scheme 1).[9] Casey and co-workers observed the hydrogen-transfer reactions of ketones and imines when **2a** was employed.[9,10] A closely related monoruthenium complex, (η^5-Ph_4C_4COH)$(CO)_2$RuCl (**2b**), was shown to exhibit a catalytic activity for the oxidation of alcohols with chloroform as an oxidant.[11] However, this oxidation also required the heating of **2b** at 90 °C and a stoichiometric amount of base under anaerobic conditions.

Shvo and co-workers have reported the reaction of the hydride-bridged complex **1** with methyl iodide to give three products: the iodide-bridged diruthenium species **4**, (η^5-Ph_4C_4COH)$(CO)_2$RuI (**2c**), and (η^5-Ph_4C_4COMe)$(CO)_2$RuI (**5**) (Scheme 2). Although they isolated **4** only in a trace amount, they succeeded in determining its molecular structure by X-ray diffraction analysis, with which they proposed that **4** is an unusual neutral complex containing two $Ru^{1/2+}$ and a single iodide bridge.[12]

We became interested in the structure of **4** and its catalytic activity because the presence of two units of **3** may greatly enhance its catalytic activity. Another interesting point is that the structure of **4** does not obey the 18-electron rule. Herein we report the formation of iodide-bridged diruthenium complex **6a** from **2c** and a dimer of **3**, [(Ph_4C_4CO)$(CO)_2Ru]_2$ (**7a**). The structure of **6a** resembles that of **4**, but obeys the 18-electron rule. Furthermore, in our present study, **6a** turned out to be a more efficient catalyst than Shvo's complex (**1**) for the oxidation of alcohols with silver oxide under mild conditions (Scheme 3). For example, 1-phenylethanol was completely oxidized within 4 h at room temperature when a catalytic amount of **6a** (2 mol % of Ru) and 1 equiv of silver oxide were used.

The reaction mixture of **2c** and **7a** in the mole ratio of 2:1 was purified by column chromatography with silica gel, and the major product was recrystallized to give X-ray quality crystals. Unexpectedly, the X-ray diffraction analysis of the

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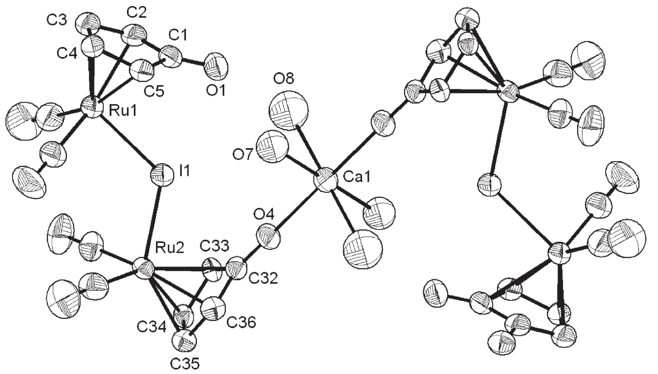
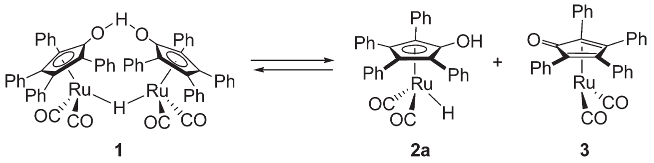
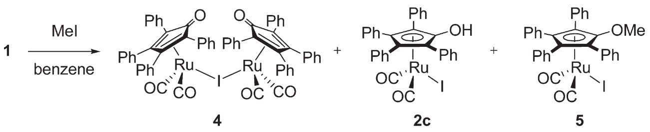


Figure 1. ORTEP drawing of **8** (50% probability). Phenyl substituents of cyclopentadienone rings, hydrogen atoms, and the cocrystallized water molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): I1−Ru1 2.6861(4), I1−Ru2 2.6848(4), Ca1−O4 2.26857(3), Ru1−C1 2.4757(4), Ru1−C2 2.2473(4), Ru1−C3 2.1866(4), Ru1−C4 2.1878(4), Ru1−C5 2.2546(4), C1−O1 1.2520(5), C32−O4 1.2568(5), Ru2−C32 2.4531(4), Ru2−C33 2.2571(4), Ru2−C34 2.1901(4), Ru2−C35 2.1922(4), Ru2−C36 2.2463(4); Ru2−I1−Ru1 126.00(2), O4−Ca1−O8 93.0(2), O4−Ca1−O7 95.5(1), O8−Ca1−O7 81.8(2).

Scheme 1. Dissociation of the Shvo Complex

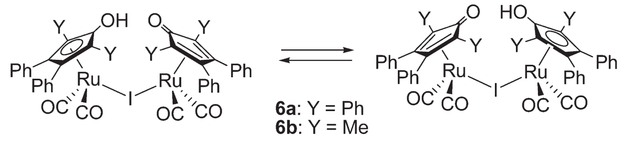


Scheme 2. Reaction of the Shvo Complex with Methyl Iodide



crystals revealed the structure of a tetranuclear ruthenium complex (**8**), which might have been formed from two units of **6a** through deprotonation and bridging with a calcium cation (Figure 1).[13] The identity of the Ca^{2+} ion was confirmed by ICP,[14] and this ion was believed to come from silica gel used for column chromatography.[15] The formal oxidation states of Ru(1), Ru(2), I, and Ca are assigned as 0, +2, −1, and +2, respectively, with which each Ru metal in **8** satisfies the 18-electron rule. The central $Ca(H_2O)_4^{2+}$ fragment formally replaces the two hydroxy protons on the Cp rings in the neighboring $[Ru_2]$ units. It is noticeable that all the bonding parameters in the I-bridged diruthenium unit of **8** are essentially the same as those of **4** reported by Shvo's group.[12,16] Subsequently, an analogue (**6b**) of **6a** could be synthesized from $[2,5\text{-}Me_2\text{-}3,4\text{-}Ph_2(\eta^5\text{-}C_4COH)(CO)_2RuI$ (**2d**) and $[2,5\text{-}Me_2\text{-}3,4\text{-}Ph_2(C_4CO)(CO)_2Ru]_2$ (**7b**) and structurally characterized by X-ray diffraction analysis (Figure 2). The molecular structure of **6b** shows clearly that a half of **7b** is bonded to the iodine atom of **2d**.

The complexes **6a** and **6b** were further characterized by IR and NMR.[16] The simple ^{13}C NMR spectra suggest their symmetrical structures; only one peak (**6a**, δ 199.4 ppm; **6b**, δ 199.9 ppm) for the carbonyl carbons was observed. Furthermore, two peaks for CO stretching (**6a**, 2026 and 1970 cm^{-1}; **6b**, 2028 and 1977 cm^{-1}) were observed in the IR spectra. Although a symmetrical structure similar to that of **1** is not plausible considering the long distance between the two oxygen atoms of the Cp rings,[17] the spectral data of **6a** and **6b** can be reasonably explained by fast proton transfer between the oxygen atoms of the Cp rings.



The catalytic activities of **6a** and **6b** were tested for the oxidation of various alcohols with silver oxide as a stoichiometric oxidant. It is worth noting that anaerobic conditions are not required for this oxidation. A combination of 2 mol % of **6a** and 1.0 equiv of Ag_2O completely oxidized 1-phenylethanol to acetophenone within 4 h at room temperature with the formation of silver mirror and Shvo's complex (**1**). In contrast, that oxidation was not possible with Ag_2O alone, and the oxidation using Shvo's complex was significantly less efficient.[18] Inorganic bases (K_2CO_3 and K_3PO_4) and metal oxides (Na_2O, Cu_2O, MgO, and ZnO) were not effective for the oxidation. The activity of our catalyst system for benzylic and aliphatic alcohols is summarized in Table 1. Secondary alcohols are converted selectively into the corresponding ketones (entries 1−3). Benzyl alcohol is oxidized into benzaldehyde in high yields (entry 4). In contrast, 1-octanol is converted into octyl octanoate (entry 5).[19] In all of the cases, the catalytic activity of **6a** is much higher than that of **6b**.

One possible mechanism for the catalytic oxidation is presented in Scheme 4. The active species **3** is liberated from **6a**. Complex **3** oxidizes alcohols to ketones with the formation of the ruthenium hydride **2a**, which is oxidized by Ag_2O with the formation of Ag metal. Meanwhile, **2c** can also participate in the catalytic cycle through the reaction with Ag_2O to generate **3**.[20] After the consumption of silver oxide, **2a** and **3** combine to form the thermodynamically stable **1**.[9a]

In summary, we have found a simple and efficient synthetic route to iodide-bridged diruthenium complexes that exhibit high catalytic activity for the oxidation of various alcohols with silver oxide under mild conditions. On the basis of the X-ray diffraction analysis for our ruthenium

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[13] Despite the presence of an intervening octahedral calcium fragment, the Ru−I−Ru bond angle (126.00(2)°) in **8** is practically the same as that (125.97(2)°) found in the analogous structure of **4** in Scheme 2.

[14] ICP analysis revealed that the calcium content of crystalline **8** is 1.51 wt %. The measured calcium content of the crystals is consistent with the calculated value (1.46 wt %) for $C_{124}H_{80}CaI_2O_{12}Ru_4 \cdot 6H_2O \cdot 2CH_2Cl_2$.

[15] The silica gel used for the purification of **6a** was analyzed by ICP, which showed the calcium content to be 0.106 wt %. When **6a** was filtered through a $CaSiO_3$ pad, **8** was obtained quantitatively.

[16] See Supporting Information.

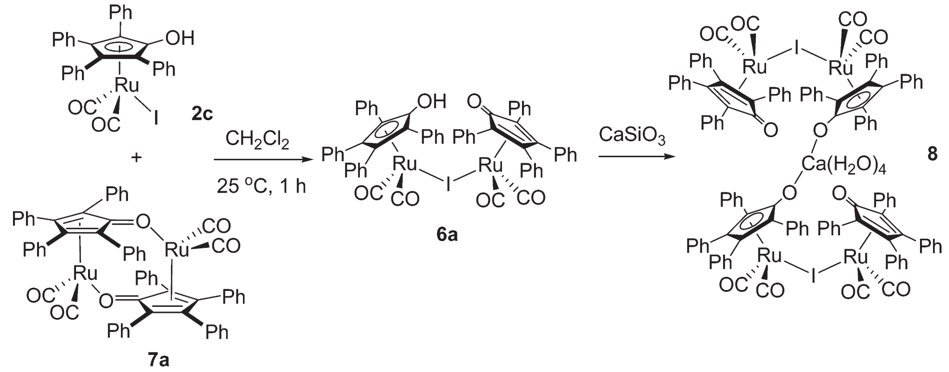
[17] The distances between two oxygen atoms of the Cp rings in **6b** and **8** are 5.44 and 4.92 Å, respectively.

[18] When 2 mol % of Shvo's complex was used in the oxidation, acetophenone was formed only in 20% yield after 3 h. However, when 1 mol % of **8** was used in the oxidation, 89% of acetophenone was formed after 3 h.

[19] Aldehyde can react with alcohol to give the corresponding hemiacetal, which is subsequently oxidized into the ester.

[20] When we used **2c** (4 mol %) instead of **6a** in the oxidation of 1-phenylethanol under the conditions of Table 1, acetophenone was obtained in quantitative yield in 3 h.

Scheme 3. Reaction of (η^5-Ph$_4$C$_4$COH)Ru(CO)$_2$I with [(Ph$_4$C$_4$CO)Ru(CO)$_2$]$_2$



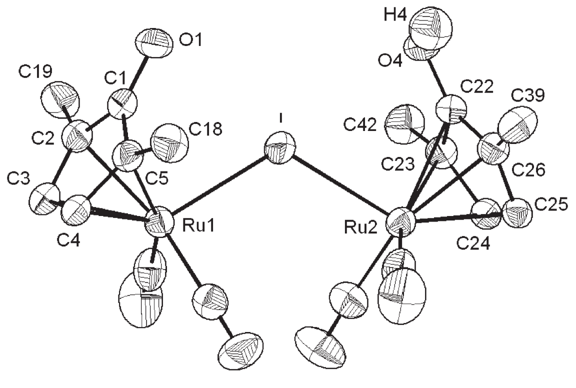


Figure 2. ORTEP drawing of **6b** (50% probability). Phenyl substituents of cyclopentadienone rings, hydrogen atoms except the hydroxyl proton, and the cocrystallized dichloromethane molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): I1−Ru1 2.7245(2), I1−Ru2 2.7062(2), Ru1−C1 2.4154(5), Ru1−C2 2.2397(5), Ru1−C3 2.1895(5), Ru1−C4 2.1959(5), Ru1−C5 2.2483(5), C1−O1 1.2844(6), C22−O4 1.3136(5), Ru2−C22 2.3580(5), Ru2−C23 2.2456(5), Ru2−C24 2.2139(5), Ru2−C25 2.1848(5), Ru2−C26 2.2529(5), Ru2−I1−Ru1 118.21(6).

complexes, we have suggested a more reasonable structure than the previous one that has been reported to contain two Ru$^{1/2+}$ centers.

Experimental Section

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under argon. Commercial chemicals were used without further purification. Flash column chromatography was carried out on silica gel (230−400 mesh) as the stationary phase. ^{1}H NMR and ^{13}C NMR spectra were recorded with a 300 MHz instrument. FT-IR spectra were obtained with KBr pellets. The ruthenium complexes, **1**,[1] **2c**,[12] **7a**,[21a] **7b**,[21a] [(η^4-Ph$_4$C$_4$CO)(CO)$_3$Ru],[21b] and [(η^4-2,5-Me$_2$-3,4-Ph$_2$C$_4$CO)(CO)$_3$Ru],[21b] were synthesized according to the literature procedures.

Synthesis of [(η^5-Ph$_4$C$_4$COH)(CO)$_2$RuIRu(η^4-Ph$_4$C$_4$CO)(CO)$_2$] (6a). In a 50 mL flask equipped with a grease-free high-vacuum stopcock, (η^5-Ph$_4$C$_4$COH)(CO)$_2$RuI (**2c**) (200.0 mg, 0.298 mmol) and [(η^5-Ph$_4$C$_4$CO)(CO)$_2$Ru]$_2$ (**7a**) (161.6 mg, 0.149 mmol) were dissolved in CH$_2$Cl$_2$ (20 mL) under argon. The solution was stirred at room temperature for 1 h. The reaction mixture was concentrated, and the resulting crude product was washed with hexane, to give **6a** as yellow-brown solid (347.5 mg, >96% yield). Mp: 162 °C dec. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.25−6.94 (m, 40H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 199.4 (Ru-CO), 132.4, 132.0, 131.8, 130.9, 130.5, 130.3, 129.4, 128.6, 128.5, 128.1, 128.1, 128.0, 127.8, 127.7, 127.4, 127.0, 101.4 (C2,5 of Cp), 87.1 (C3,4 of Cp). IR (KBr, cm^{-1}): ν(CO) 2026 (s), 1970 (s). FAB MS: *m*/*z* 1213.0 (M + H).

Synthesis of [2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$COH)](CO)$_2$RuI (2d). In a 50 mL flask equipped with a grease-free high-vacuum stopcock, [2,5-Me$_2$-3,4-Ph$_2$(η^4-Ph$_4$C$_4$CO)]Ru(CO)$_3$ (250 mg, 0.561 mmol) and CHI$_3$ (1.5 equiv) were dissolved in 2-propanol (5 mL) and toluene (15 mL) under argon. The solution was heated to reflux for 10 h. The reaction mixture was concentrated, and the resulting crude product was purified by column chromatography (hexane/ethyl acetate = 1:1) to give **2d** as an orange solid (292 mg, 95% yield). Mp: 168 °C dec. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.27−7.15 (m, 10H), 2.12 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 197.9 (Ru-CO), 134.2 (C1 of Cp), 131.6, 129.8, 128.8, 128.4, 101.4 (C2,5 of Cp), 87.0 (C3,4 of Cp), 9.6 (CH$_3$ of C2,5). IR (KBr, cm^{-1}): ν(CO) 2026 (s), 1973 (s). MS (FAB, *m*/*z*): 545.9 (M$^+$). Anal. Calcd for C$_{21}$H$_{17}$IO$_3$Ru: C, 46.25; H, 3.14. Found: C, 46.39; H, 3.26.

Synthesis of [(η^5-2,5-Me$_2$-3,4-Ph$_2$C$_4$COH)(CO)$_2$RuIRu(η^4-2,5-Me$_2$-3,4-Ph$_2$C$_4$CO)(CO)$_2$)] (6b). In a 50 mL flask equipped with a grease-free high-vacuum stopcock, [2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$COH)](CO)$_2$RuI (**2d**) (100.0 mg, 0.183 mmol) and [(Me$_2$Ph$_4$C$_4$CO)(CO)$_2$Ru]$_2$ (**7b**) (76.4 mg, 0.091 mmol) were dissolved in CH$_2$Cl$_2$ (20 mL) under argon. The solution was stirred at room temperature for 1 h. The reaction mixture was concentrated, and the resulting crude product was washed with hexane, to give **6b** as a yellow-brown solid (161 mg, >91% yield). Mp: 157 °C dec. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.19 (s, 20H) 2.22 (s, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 199.9 (Ru-CO), 153.6 (C1of Cp), 131.4, 130.9, 128.2, 128.1, 100.9 (C2,5 of Cp), 84.7 (C3,4 of Cp). IR (KBr, cm^{-1}): ν(CO) 2028 (s), 1977 (s). FAB MS: *m*/*z* 964.9492 (M + H).

Synthesis of [(η^4-Ph$_4$C$_4$CO)(CO)$_2$RuIRu(η^4-Ph$_4$C$_4$CO)(CO)$_2$]$_2$-Ca(H$_2$O)$_4$ (8). In a 10 mL flask equipped with a grease-free high-vacuum stopcock, (η^5-Ph$_4$C$_4$COH)(CO)$_2$RuI (100 mg, 0.073 mmol) and [(Ph$_4$C$_4$CO)Ru(CO)$_2$]$_2$ (85 mg, 0.073 mmol) were dissolved in dichloromethane (10 mL) under argon. The solution was stirred at room temperature for 6 h. The reaction mixture was concentrated, and the resulting crude product was purified by column chromatography (hexane/ethyl acetate = 1:1) to give **8** as a yellow solid (170 mg, 95% yield). Mp: 198 °C dec. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.21−6.97 (m, 80H), δ 2.99 (s, 8H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 200.13 (Ru-CO), 132.1, 131.8, 131.6, 127.8, 127.6, 126.8 (C1 of Cp), 101.2 (C2,5 of Cp), 84.3 (C3,4 of Cp). IR (KBr, cm^{-1}): ν(CO) 3425 (b), 2023 (s), 1979 (s), 1545 (s).

Structure Analysis of [(η^4-Ph$_4$C$_4$CO)(CO)$_2$RuIRu(η^5-Ph$_4$C$_4$-CO)(CO)$_2$]$_2$Ca(H$_2$O)$_6$(CH$_2$Cl$_2$)$_2$. The crystal was obtained by layering of hexane into a dichloromethane solution of the complex. A suitable crystal was mounted onto a specially

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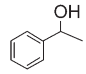
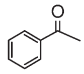
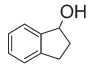
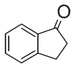
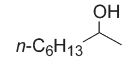
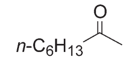
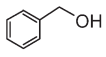
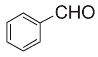
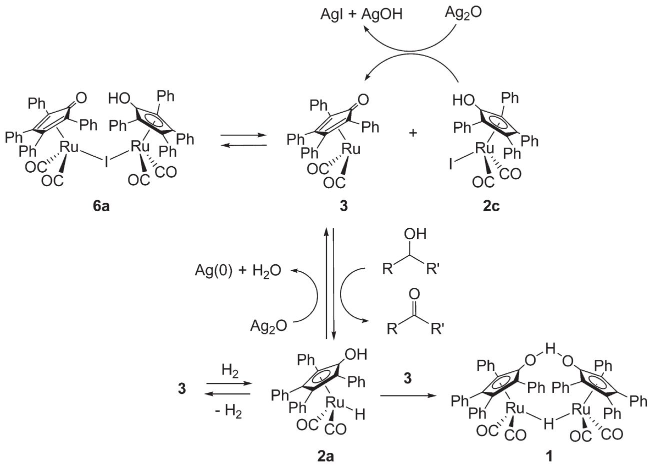
[21] (a) Mays, M. J.; Morris, M. J.; Raithby, P. R.; Shvo, Y.; Czarkie, D. *Organometallics* **1989**, *8*, 1162. (b) Bruce, M. I.; Knight, J. I. *J. Organomet. Chem.* **1968**, *12*, 412.

Table 1. Oxidation of Alcohols[a]

Entry	Substrate	Product	6a		6b	
			Time (h)	Yield (%)[b,c]	Time (h)	Yield (%)[b,c]
1			4.0	>99 (97)	10	86 (85)
2			3.0	>99 (98)	10	98 (95)
3			3.0	>99 (98)	10	85 (83)
4			3.0	93 (90)	10	88 (85)
5	n-$C_8H_{17}OH$	n-$C_7H_{15}CO_2$-nC_8H_{17}	3.0	90 (90)	10	86 (84)

[a] Alcohol (0.25 mmol) was added to a suspension of **6** (2.0 mol %) and Ag_2O (1.0 equiv) in CH_2Cl_2 (0.5 mL), and the resulting mixture was stirred at room temperature in air. [b] Determined by GC. [c] Numbers in parentheses show isolation yields.

Scheme 4. Proposed Pathway for the Ru-Catalyzed Oxidation of Alcohols



constructed apparatus with cooling in an inert atmosphere on a diffractometer and analyzed. Structure solution and refinement was carried out with the SHEKXLX programs. Crystal data for **8**: $C_{126}H_{96}CaCl_4I_2O_{18}Ru_4$, M_w 2737.99, brown, crystal size (0.32 × 0.28 × 0.26), monoclinic, space group $P2_1/n$, $a = 15.6348(2)$ Å, $b = 16.9401(2)$ Å, $c = 23.1628(3)$ Å, $\alpha = 90°$, $\beta = 95.5930(10)°$, $\gamma = 90°$, $V = 6105.58(13)$ Å^3, $Z = 2$, $D_{calcd} = 1.486$ g cm^{-3}, $F(000) = 2720$, $T = 296(2)$ K, $\mu = 1.183$ mm^{-1}, 119 601 measured reflections, 15 021 unique reflections ($R_{int} = 0.0414$), minimum/maximum transmission factors 0.7485/0.7034. The final agreement factors were R1 = 0.0482 ($I > 2\sigma(I)$ and wR2 = 0.1194, with 15 021/0/680 data/restraints/parameters and GOF = 1.024. The largest peak and hole were 1.282 and −0.724 e/Å^3.

Structure Analysis of $[(\eta^5\text{-}2,5\text{-}Me_2\text{-}3,4\text{-}Ph_2C_4COH)(CO)_2RuIRu(\eta^4\text{-}2,5\text{-}Me_2\text{-}3,4\text{-}Ph_2C_4CO)(CO)_2](CH_2Cl_2)_2$. The crystal was obtained by layering of hexane into a dichloromethane solution of the complex at −40 °C. A suitable crystal was mounted onto a specially constructed apparatus with cooling in an inert atmosphere on a diffractometer and analyzed. Structure solution and refinement was carried out with the SHEKXLX programs. Crystal data for **6b**: $C_{44}H_{37}Cl_4IO_6Ru_2$, M_w 1132.58, yellow-brown, crystal size (0.28 × 0.22 × 0.18), monoclinic, space group $P_{1}2_{1}/c_{1}$, $a = 16.104(14)$ Å, $b = 16.875(15)$ Å, $c = 17.228(15)$ Å, $\alpha = 90°$, $\beta = 104.437(15)°$, $\gamma = 90°$, $V = 4534(7)$ Å^3, $Z = 4$, $D_{calcd} = 1.659$ Mg m^{-3}, $F(000) = 2232$, $T = 243(2)$ K, $\mu = 1.627$ mm^{-1}, 26 009 measured reflections, 9255 unique reflections ($R_{int} = 0.0345$), minimum/maximum transmission factors 0.7583/0.6586. The final agreement factors were R1 = 0.0456 ($I > 2\sigma(I)$ and wR2 = 0.1327, with 9255/0/519 data/restraints/parameters and GOF = 1.015. The largest peak and hole were 2.065 and −1.130 e/Å^3.

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Supporting Information Available: Experimental procedures, characterization data for **2c**, **2d**, **6a**, **6b**, **7a**, **7b**, and **8**; summaries of structure determination and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for **8** and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.