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Alternative Synthesis and Fluxional Behavior of *triangulo*-$Os_2Rh(CO)_9(C_5R_5)$ (R = H, Me)

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Thermal reaction between $Os_2(CO)_8(\mu\text{-}C_2H_4)$ and $(C_5R_5)Rh(CO)_2$ provides a convenient alternative synthesis of the *triangulo*-$Os_2Rh(CO)_9(C_5R_5)$ complexes (R = H (**2a**), Me (**2b**)). In solution the molecules are fluxional. The mechanism and energetics of the carbonyl exchange processes have been investigated by VT ^{13}C NMR spectroscopy. For **2a** a near low temperature limiting spectrum is obtained at −115 °C, which is consistent with the known solid-state structure of the complex. Carbonyl exchange in **2a** is initiated between the Os and Rh centers; the associated $\Delta G^{\ddagger}$ is 8.4 (4) kcal mol^{-1} at −80 °C. The same process is still fast in **2b** even at −100 °C and results in an intermediate averaged spectrum. At higher temperatures global exchange of CO groups over the three metal centers is seen in **2b**; $\Delta G^{\ddagger}$ = 12.7 (2) kcal mol^{-1} at 22 °C. The difference in fluxionality of **2a** and **2b** is explained in terms of the greater electron-releasing nature of the C_5Me_5 moiety.

Introduction

The concept of isolobal analogy, initially proposed by Hoffmann,[1] has been beautifully exploited by Stone and his school in the rational synthesis of heteronuclear metal–metal-bonded species.[2] As illustrated by Stone, the isolobal mapping

$$CpRh(CO) \leftarrow\!\!\!\circ\!\!\!\rightarrow Fe(CO)_4 \leftarrow\!\!\!\circ\!\!\!\rightarrow CH_2$$

led to the synthesis of a variety of heterobimetallic complexes such as $[MnRh(\mu\text{-}CO)_2(C_5H_5)(C_5Me_5)]$ and $[FeRh(\mu\text{-}CO)_2(CO)_4(C_5Me_5)]$[3] and $[CrRh(\mu\text{-}CO)_2(CO)_2(C_5Me_5)(arene)]$,[4] whereas the isolobal relation $CpRh(\mu\text{-}CO)_2RhCp \leftarrow\!\!\!\circ\!\!\!\rightarrow H_2C{=}CH_2$ suggested the preparation of the trimetallic complexes $[Pt\{Rh_2(\mu\text{-}CO)_2(C_5Me_5)\}_2]$[5] and $[MRh_2(\mu\text{-}CO)_2(CO)_5(C_5Me_5)_2]$ (M = Cr, Mo, W).[6]

Recent reports from this laboratory disclosed a convenient photochemical synthesis of diosmacyclobutane,[7] $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CH_2)$ (**1**), and presented evidence for facile cycloreversion[8,9] in this molecule (Scheme I). The unsaturated $Os_2(CO)_8$ fragment, obtained from fragmentation of the Os_2C_2 ring, is also isolobal with ethylene and clearly could be used as a building block for the synthesis of osmium-containing heterometallic complexes.

Since in its reaction with unsaturated organic substrates the $Os_2(CO)_8$ unit appeared to prefer the 2 + 2 cycloaddition mode, it was of interest to investigate the possible cycloaddition between the two isolobal dimetallic analogues of ethylene $Rh_2(C_5R_5)_2(CO)_2$ and $Os_2(CO)_8$, with a view to prepare the hitherto unknown saturated tetranuclear cluster $Rh_2Os_2(C_5R_5)_2(CO)_{10}$.[10] Unfortunately, as shown in Scheme II, the reaction did not take this course but gave instead the known trinuclear cluster **2a**.[11] In view of this result the more rational reaction, that between **1** and $(C_5R_5)Rh(CO)_2$ (R = Me, H), was also carried out and gave **2** (R = H (**2a**), Me (**2b**)) in moderate yields. Since the fluxional behavior of **2a** was left unresolved by Shore et al.,[11] we decided to carry out a detailed variable-temperature (VT) ^{13}C NMR study on both compounds and the results of this analysis are also reported.

Results and Discussion

$$\underset{\mathbf{1}}{Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}H_2CCH_2)} + (C_5R_5)Rh(CO)_2 \xrightarrow[45\text{-}50\ ^\circ C,\ 16\ h]{hexane} Os_2Rh(CO)_9(C_5R_5) \quad (1)$$

R = H, **2a** (67%)
R = Me, **2b** (61%)

Previously **2a** was synthesized by the reaction of $H_2Os_3(CO)_{10}$ with $(C_5H_5)Rh(CO)_2$ in toluene at 90 °C for 3 days. Not surprisingly, the formation of **2a** from **1** proceeds more readily and more cleanly (eq 1). Although the reaction is accompanied by the formation of some byproducts, **2a** can be simply recovered by short-path column chromatography with pentane as eluant. Reaction with $(C_5Me_5)Rh(CO)_2$ gives the analogous **2b**. As reported by Shore et al.,[11] the compounds are air-stable red solids. The mass spectra of the compounds are in accord with the molecular formulation and feature sequential loss of nine CO ligands. The infrared spectra of the molecules show eight terminal carbonyl bands, which is not unexpected from the low molecular symmetry. The positions of the bands of **2a** are in reasonable agreement with the reported values,[11] there being a shift to higher frequencies by some 5–10 cm^{-1}. The larger number of bands observed by us is presumably due to the better sensitivity and resolution provided by our FT-IR machine. The solid-state structure of **2a** was determined by X-ray crystallography.[11] A schematic view of the molecular structure and those proposed for the related $Fe_2Rh(CO)_9(C_5H_5)$[3,12] and $Fe_2Co(CO)_9(C_5H_5)$[13] are shown in Figure 1. It is interesting to note that, whereas **2a** has only terminal carbonyls, the last two

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[1] Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

[2] Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89.

[3] Aldride, M. L.; Green, M.; Howard, J. A. K.; Pain, G. N.; Porter, S. J.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1333.

[4] Bau, R. D.; Green, M.; Marsden, K.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 507.

[5] Green, M.; Howard, J. A. K.; Pain, G. N.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1327.

[6] Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 759.

[7] (a) Burke, M. R.; Takats, J.; Grevels, F.-W.; Reuvers, J. G. A. *J. Am. Chem. Soc.* **1983**, *105*, 4092. (b) Ball, R. G.; Burke, M. R.; Cowie, M.; Takats, J. Manuscript in preparation.

[8] (a) Takats, J. *Polyhedron* **1988**, *7*, 931. (b) Burke, M. R.; Seils, F.; Takats, J. *Organometallics*, submitted for publication.

[9] Elegant experiments have been carried out to probe the mechanism of the cycloreversion process: Hembre, R. T.; Scott, C. P.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3468.

[10] The isoelectronic $Os_4(CO)_{16}$ has been reported: Johnston, V. J.; Einstein, F. W.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1987**, *109*, 8111.

[11] Hsu, L.-Y.; Hsu, W.-L.; Jan, D.-Y.; Marshall, A. G., Shore, S. G. *Organometallics* **1984**, *3*, 591.

[12] (a) Knight, J.; Mays, M. J. *J. Chem. Soc. A* **1970**, 654. (b) Howell, J. A. C.; Matheson, T. W.; Mays, M. J. *J. Organomet. Chem.* **1975**, *88*, 363.

[13] An identical structure was assumed for the analogous $Fe_2Rh(CO)_9(C_5Me_5)$: Aldridge, M. L.; Green, M.; Howard, J. A. K.; Parin, G. N.; Porter, S. J.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1333.

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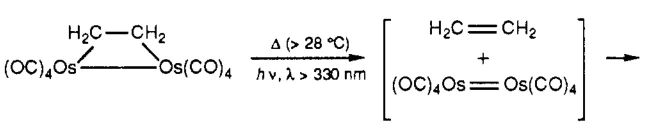
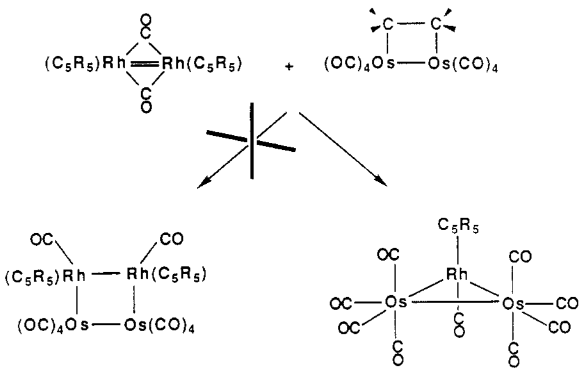
Scheme I



Scheme II



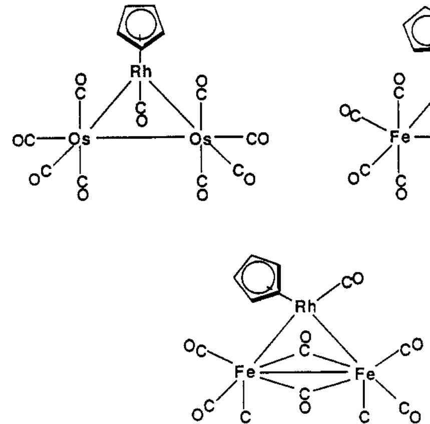


Figure 1. Schematic diagrams of the structures of $Os_2Rh(CO)_9(C_5H_5)$, $Fe_2Co(CO)_9(C_5H_5)$ and $Fe_2Rh(CO)_9(C_5H_5)$.

compounds also possess two bridging carbonyls. This is in accord with the well-known greater propensity of first-row transition elements to support bridging carbonyl units[14] compared to their heavier congeners. Of importance for the fluxional behavior of **2a** and **2b** is the postulate that, in the *triangulo*-Fe_2Co complex, the bridging carbonyls are situated between the two different metals.

Fluxional Behavior of 2a and 2b. In accord with previous observation we find **2a**, and also **2b**, to be fluxional in solution. The variable-temperature ^{13}C NMR spectra of **2a** and **2b**, in the carbonyl region, are shown in Figures 2 and 3, respectively. The spectra of **2a** were recorded on a sample highly enriched in ^{13}CO.

In our hands the ^{13}C NMR spectrum of **2a** (enriched in ^{13}CO) at room temperature shows not one[11] but two resonances at 185.5 and 173.5 ppm in a 7:2 intensity ratio; however, the lower intensity signal is easily missed. Samples containing only natural-abundance ^{13}CO show this resonance only after a large number of accumulations. This may have been the reason for the previously reported single line by Shore et al.[11] As the temperature is lowered, the major signal broadens, disappears into the base line at −80 °C, and reappears as three new signals. Although the low-temperature limiting spectrum has not yet been reached by −115 °C, reliable integration of the resonances could be obtained and this establishes that the resonances are in the ratio 1:4:2:2. From the C_s molecular symmetry of **2a**[11] five resonances, in the ratio 1:2:2:2:2, are expected. To account for the slight discrepancy, we assume that the chemical shifts of two resonances in **2a** are nearly identical. Indeed, close examination of the signal with a relative intensity of 4 reveals that it is not a single peak but consists of two closely spaced lines separated by 26 Hz. Therefore, there is very little doubt that the instantaneous solution structure of **2a**, as revealed by the ^{13}C NMR spectrum at −115 °C, is the same as the solid-state structure reported by Shore et al.[11] In particular, the lowest field resonance of intensity 1 is assigned to the unique CO on rhodium. Its position, at 197.3 ppm, is in the region typical of terminal rhodium carbonyls, and its doublet appearance is due to characteristic $^{1}J_{^{103}Rh-^{13}C}$ coupling (77 Hz).[15] We defer assignments of the remaining resonances until after the discussion of the mechanism of carbonyl migration.

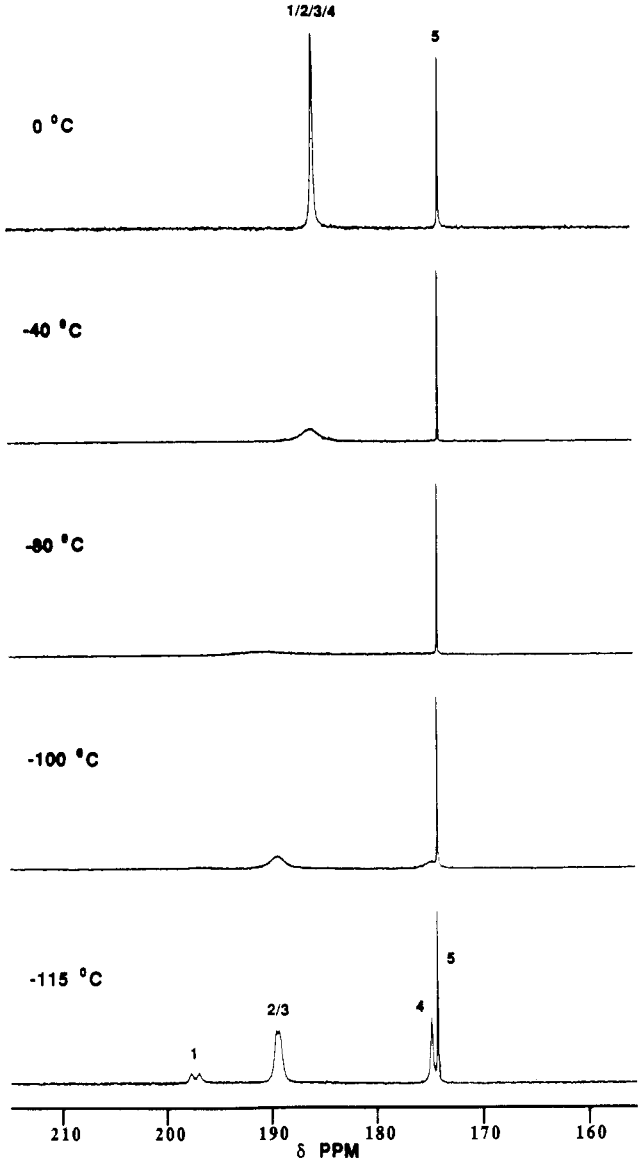


Figure 2. Variable-temperature ^{13}C NMR spectra of $Os_2Rh(CO)_9(C_5H_5)$ (**2a**) in the carbonyl region in THF-d_8.

As seen in Figure 3, the ^{13}C NMR spectrum of **2b** shows only two carbonyl signals in a 7:2 intensity ratio even at

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[14] (a) Kawaguchi, S. *Variety in Coordination Modes of Ligands in Metal Complexes*; Springer-Verlag: New York, 1987; p 1333. (b) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1.

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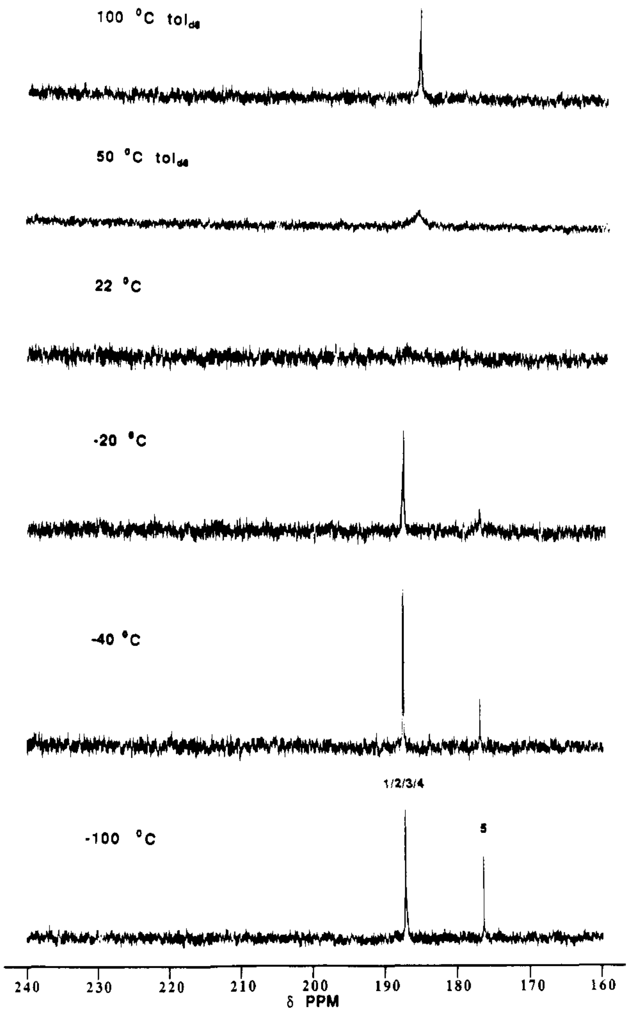
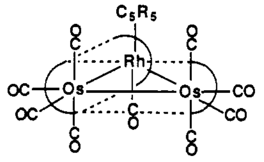


Figure 3. Variable-temperature ^{13}C NMR spectra of $Os_2Rh(CO)_9(C_5Me_5)$ (**2b**) in the carbonyl region (T = +22 to -100 °C in CD_2Cl_2, T = 50 and 100 °C in toluene-d_8).

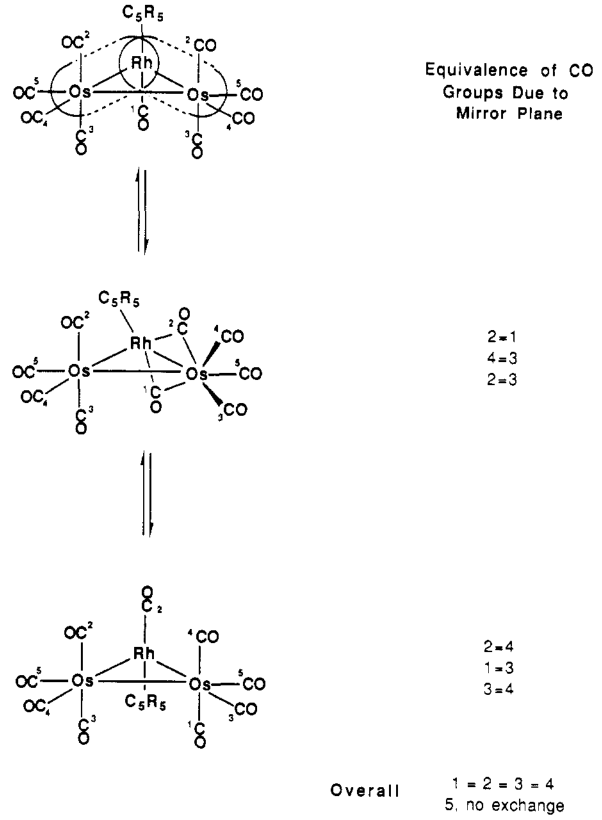
Chart I



-100 °C. This clearly indicates that the exchange process that averages seven carbonyl groups is much more facile in this molecule than in **2a**. Above -20 °C the two resonances broaden, and at room temperature they have coalesced into the base line. This heralds the onset of global exchange of carbonyl groups over the three metal centers. The high-temperature limiting spectrum, at +100 °C, shows a single sharp resonance. The position of this signal, 184.2 ppm, is in excellent agreement with the weighted average of 184.2 ppm.

A mechanism that accounts for the observed line shape changes in **2a** and in **2b** is the well-documented pairwise terminal-bridge carbonyl exchange.[16] Applied to triangular clusters, the operation of this process requires the presence of carbonyl groups that are roughly coplanar. As shown in Chart I, in compounds **2** there are three such vertical planes that satisfy the above requirement. The Os-Os plane contains six carbonyl groups, whereas the two Os-Rh planes, rendered equivalent by the C_s molecular symmetry, each contain four carbonyl ligands, three from osmium and one from rhodium. The latter CO group is common to both planes.

Scheme III. Pairwise CO Exchange in the Os-Rh Plane



Clearly a satisfactory explanation for the low-temperature line shape changes in **2a** is that the carbonyl groups exchange in the two vertical Os-Rh planes. As shown in Scheme III, this process leads to the averaging of seven carbonyl moieties and leaves the carbonyl ligands trans to the Os-Os bond, namely the carbonyls labeled CO(5), invariant and therefore accounts for the lack of line broadening of one signal of intensity 2 throughout the low-temperature exchange process. For this reason the resonance at δ 174.1 ppm is assigned to CO(5). We suggest that the signal of intensity 2, close to this resonance, at δ 174.7 ppm is most reasonably assigned to carbonyls labeled CO(4), the ligands trans to the Rh-Os bonds, because of the similarity of their chemical environments to that of CO(5). This leaves the two closely spaced peaks at δ 189.5 and 189.2 ppm belonging to the trans-CO groups on osmium, CO(2) and CO(3).

It is interesting, albeit not unexpected, that the low-temperature process consists of carbonyl migration between the different metal atoms, Rh and Os, and not between the two osmium centers. This observation is in accord with the greater reluctance of the third-row transition metals to support bridging carbonyl groups,[14] necessary for the fluxional process, and with the well-known increase in activation energy for bridge-terminal carbonyl exchange as a metal triad is descended.[17] However, the influence of the heteronuclear metal-metal bond on the

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(16) (a) Adams, R. D.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6589. (b) Bond, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639. (c) Johnson, B. F. G.; Benfield, R. E. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chichester, England, 1980; p 471.

(17) Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 3, p 89 and references therein.

fluxional process cannot be ignored. Indeed we have already remarked that in the related $Fe_2Co(CO)_9(C_5H_5)$ molecule the two bridging carbonyls are situated between Fe and Co and not between the two iron centers. Detailed studies by Geoffroy[18] on carbonyl scrambling processes in heterometallic clusters also showed that the low-energy process involves bridge–terminal CO exchange initiated on the first-row metal prior to more extensive cluster carbonyl movements (cf. $H_2FeM_3(CO)_{13}$; M = Ru, Os[18b]). In addition, enhanced substitutional lability of the CO ligands in heterometallic clusters is also well documented.[19]

The activation parameters for the low-temperature carbonyl scrambling in **2a**, as determined by spectral simulation, which also confirmed the proposed mechanism, are $\Delta H^{\ddagger} = 6.1$ (3) kcal mol^{-1}, $\Delta S^{\ddagger} = -12.6$ (5) eu, and $\Delta G^{\ddagger} = 8.4$ (4) kcal mol^{-1} (at −80 °C, the coalescence temperature). The facility of this process is much greater in **2b** (see Figure 2). This is consonant with previous observations, where it is normally observed that replacement of a ligand by a better donor functionality (C_5H_5 by C_5Me_5 in the present context) lowers the barrier for carbonyl group migration.[20] Compound **2b** also features global CO exchange over the three metal centers at higher temperature. This is most readily explained by invoking carbonyl movements in the third allowed plane, i.e., the vertical Os–Os plane. The activation energy for carbonyl migration over the two osmium centers is calculated to be 12.7 (2) kcal mol^{-1} (at 22 °C), a value that is lower than the barrier to the exchange in $Os_3(CO)_{12}$,[21] ca. 17 kcal mol^{-1}. This indicates that the electronic effect of the $(C_5Me_5)Rh(CO)$ group is transmitted to the Os–Os plane, the net result being that of electron donation.

Experimental Section

All manipulations were performed under a static atmosphere of rigorously purified nitrogen or argon, with use of standard Schlenk techniques. Solvents were dried by refluxing under nitrogen with an appropriate drying agent and distilled just prior to use.

The compounds $(C_5H_5)Rh(CO)_2$,[22] $(C_5Me_5)Rh(CO)_2$,[23] and $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)$[7] were prepared by published procedures. Enrichment of the last compound in ^{13}CO was achieved by carrying out the photoreaction between C_2H_4 and ^{13}CO-enriched $Os_3(CO)_{12}$ (level of enrichment ca. 50%, as determined by mass spectrometry).

Infrared spectra were obtained with a Nicolet MX-1 FT-IR spectrometer. NMR spectra were recorded on a Bruker WP-400 spectrometer. Variable-temperature studies were obtained with samples sealed with a serum septum or under vacuum. Temperature calibration was made with a copper/constantan thermocouple. Free energy of activation at the coalescence temperature, $\Delta G^{\ddagger}_{T_c}$, was calculated by using the approximate expression applicable to the two-site exchange problem.[24] For the more complicated behavior involving four exchanging sites, the low-temperature process for **2a**, rates of exchange were obtained by visual comparison of the observed and computer-simulated spectra. Computer simulation was achieved with a local program written by Professor McClung of this department. Mass spectra were taken with an AEI MS-12 spectrometer operating at 70 or 16 eV. The samples were introduced into the ion source by using the direct inlet technique at a temperature just sufficient to record the spectrum. Elemental analyses were performed by the Microanalytical Laboratory of this department.

Synthesis of $Os_2Rh(CO)_9(C_5H_5)$ (2a). $Os_2(CO)_8(\mu\text{-}C_2H_4)$ (33.9 mg, 0.054 mmol) was placed in a 50-mL three-neck flask equipped with a condenser. The flask was evaculated and filled with argon three times. Next, 15 mL of hexane and 0.60 mL of a 2.4 mg/mL hexane solution of $(C_5H_5)Rh(CO)_2$ (14.4 mg, 0.064 mmol) were added and the solution was heated, with stirring, at 45–50 °C for 16 h. Solvent was removed in vacuo. The solid residue was dissolved in a minimum volume of CH_2Cl_2, and the solution was loaded onto a 5-cm bed of silica gel. Elution with pentane caused the development of an orange band; a yellow immobile band remained on top of the column. Solvent was removed from the eluant in vacuo, and the residue was recrystallized from pentane at −80 °C to give 28.9 mg (67%) of red, air-stable crystals of **2a** (mp 140–142 °C dec). Anal. Calcd for $C_{14}H_5O_9Os_2Rh$: C, 21.00; H, 0.63. Found: C, 21.17; H, 0.59. Infrared spectrum (pentane, 25 °C, ν_{CO}): 2106 m, 2060 s, 2027 s, 2015 vs, 2009 sh, 1997 sh, 1984 w, 1967 w cm^{-1} (in cyclohexane 2105 m, 2058 s, 2025 s, 2014 vs, 2008 sh, 1996 s, 1983 w, 1966 w cm^{-1}). ^1H NMR ($CDCl_3$, 25 °C) δ 5.52 (s, C_5H_5). ^{13}C NMR (THF-d_8): 25 °C, 185.6 (s, 7 CO), 173.6 (s, 2 CO); −115 °C, 197.3 (d, $J_{Rh-C} = 77$ Hz, 1 CO, CO_{Rh}), 189.5/189.2 (s, 2 CO/2 CO), 174.7 (s, 2 CO), 174.1 (s, 2 CO). Mass spectrum (70 eV, 100 °C, m/e): $M^+ - nCO$, $n = 0$–9. Rate data (k (s^{-1})/T (K)): 20/158, 150/173, 1500/193, 8500/233, 200000/273.

Synthesis of $Os_2Rh(CO)_9(C_5Me_5)$ (2b). The synthesis followed the same path as for **2a**. $Os_2(CO)_8(\mu\text{-}C_2H_4)$ (22.5 mg, 0.036 mmol) and $(C_5Me_5)Rh(CO)_2$ (11.6 mg, 0.039 mmol) gave 18.6 mg (61%) of red, air-stable crystals of **2b** (mp 191–193 °C dec). Anal. Calcd for $C_{19}H_{15}O_9Os_2Rh$: C, 26.21; H, 1.74. Found: C, 26.52; H, 1.79. Infrared spectrum (pentane, 25 °C, ν_{CO}): 2097 m, 2050 s, 2018 s, 2007 s, 1999 w, 1987 m, 1974 w, 1953 w cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 1.88 (s, C_5Me_5). ^{13}C NMR (CD_2Cl_2, −100 °C): δ 186.7 (d, $J_{Rh-C} = 9$ Hz, 7 CO), 175.3 (s, 2 CO). Mass spectrum (16 eV, 160 °C, m/e): $M^+ - nCO$, $n = 0$–9.

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[20] Often such replacements involve CO by PR_3 type ligands; see for example: Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437.

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