Relationships between Structure and Ligand Dynamics in Organometal Clusters

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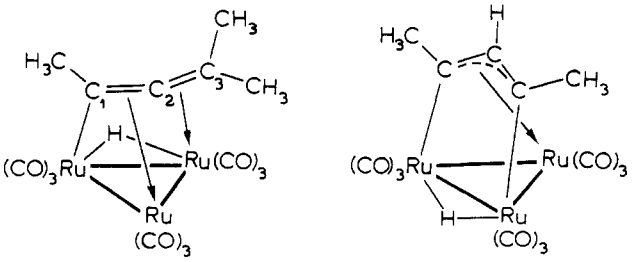
The variable-temperature ^1H and ^{13}C NMR spectra of the hydrido organometal clusters $HM_3(CO)_9[CH_3C{=}C{=}C(CH_3)_2]$ (M = Ru, Os) have been examined. When M ≈ Ru, a dynamic process is observed which averages the magnetically inequivalent methyl groups on the ligand and also results in a twofold symmetry plane at the metal cluster with respect to the carbonyl ligands. These observations are explained in terms of edge hopping of the hydride ligand and a simultaneous "wagging" motion of the organic ligand. For the osmium derivative the barrier to the motion of the organic ligand is higher, but it cannot be established whether it is directly coupled with the edge-hopping of the hydride. For comparison, the variable-temperature ^{13}C NMR spectrum of $HRu_3(CO)_9(CH_3CCHCCH_3)$ was investigated. Here, no motion of the organic ligand could be detected although opening of the hydride bridge appears to be occurring as evidenced by the different barriers to axial–radial CO site exchange at the different ruthenium atoms. The phosphine derivative $HRu_3(CO)_8P(C_6H_5)_3(CH_3CCHCCH_3)$, in which the phosphine is bound to the metal atom which is σ-bound to the organic ligand, shows a higher barrier to axial–radial site exchange at the hydride-bridged metal atoms.

Introduction

Although there have been numerous investigations of ligand mobility in metal clusters by NMR techniques, the relationships between the motions of different types of ligands on the same metal cluster have not been clearly delineated in many cases.[1] This is particularly true in the case of hydrido organometal clusters where a wide variety of bonding modes of the organic ligand to the metal cluster have been observed.[2] We have recently completed a detailed investigation of the ligand dynamics in $HRu_3(CO)_9[C_2C(CH_3)_3]$ where two carbon atoms are bound to a trimetallic cluster, and our evidence indicates that the organic ligand is static in this species.[3–5] Shapley and co-workers have shown that σ–π interconversion of the organic ligand in $HOs_3(CO)_{10}(CH{=}CHR)$ is independent of other ligand migrations in the molecule.[6] Additionally, it has been suggested that an oscillating motion of the organic ligand in $H_2Os_3(CO)_9$ ($R'C{\equiv}CR$) along with hydride migration around the metal triangle (which must be at least as fast but now slower than the oscillation of the organic ligand) and axial–radial exchange of the carbonyl ligands can fully explain the observed dynamic behavior in this class of compounds.[7–9] For the isomeric complexes $H_2Os_3(CO)_9(C{=}CH_2)$ edge migration of one hydride is thought to average the magnetically inequivalent protons on the organic ligand while at higher temperatures migration of both hydrides is observed.[10,11] The relationship of the CO migrations to these two hydride–exchange processes remains unclear, and the organic ligand appears to be static in these complexes as well. Thus for two carbon fragments bound to trimetallic sites, the nature of the ligand-exchange processes observed does vary with the structure of the organic ligand. We report here the initial results of our investigation of the relationships between ligand migrations in hydrido organometal clusters where three carbon fragments are bound to a trimetallic site by two different metal carbon frameworks, Ia and II.



Ia II

Previously it has not been possible to compare the dynamic NMR spectra of these structural types since I isomerizes to II when one of the substitutents on the C(3)

(1) "Transition Metal Clusters", B. F. G. Johnson, Ed., Wiley, New York, 1980.
(2) A. P. Humphries and H. D. Kaesz, *Prog. Inorg. Chem.*, **25**, 146 (1979).
(3) R. Fahmy, K. King, E. Rosenberg, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Am. Chem. Soc.*, **102**, 3626 (1980).
(4) C. Barner Thorsen, K. I. Hardcastle, E. Rosenberg, J. Siegel, A. M. Manotti Lanfredi, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chem.*, **20**, 4306 (1981).
(5) C. Barner Thorsen, E. Rosenberg, S. Aime, D. Osella, and L. Milone, manuscript in preparation.
(6) J. R. Shapely, S. I. Richter, M. Tachikawa, and J. B. Keister, *J. Organomet. Chem.*, **94**, C43 (1975).
(7) J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Organomet. Chem.*, **97**, C16 (1975).
(8) A. J. Deeming, *J. Organomet. Chem.* **150**, 123 (1978).
(9) S. Aime and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, in the press.
(10) A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.* 1415 (1974).
(11) W. G. Jackson, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, **90**, C13 (1975).

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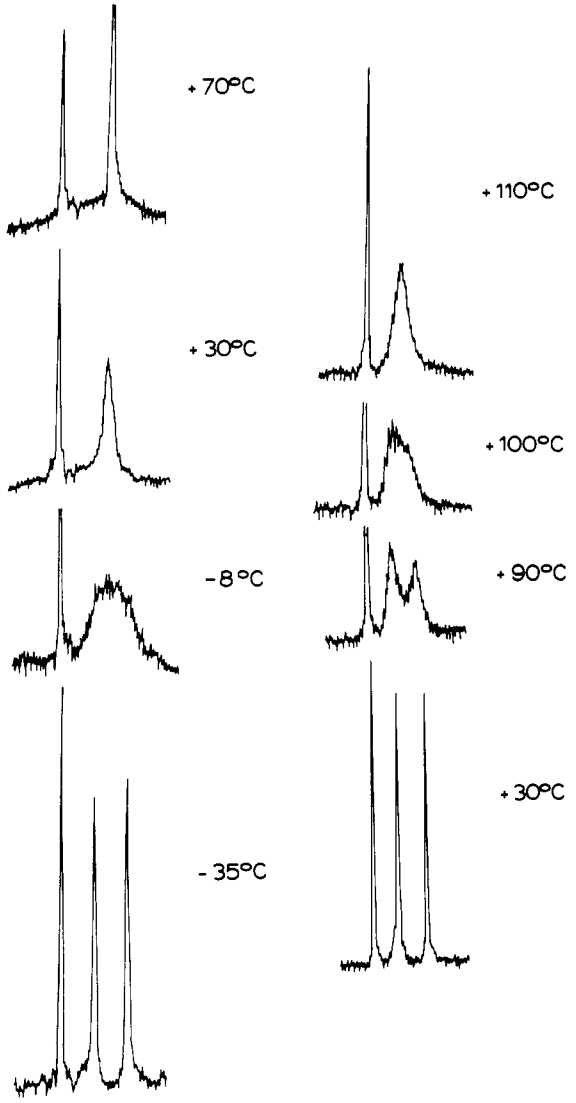


Figure 1. Variable-temperature ^{1}H NMR spectra of $HM_3(CO)_9[CH_3C{=}C{=}C(CH_3)_2]$ (M = Ru (Ia, left) and Os (Ib, right)) in the aliphatic region.

carbon of the allene is hydrogen.[12] We recently found that the reaction of $M_3(CO)_{12}$ (M = Ru, Os) with 4-methyl-2-pentyne gives I which does not isomerize.[13]

Results and Discussion

(A) Allenic Derivatives. The reaction of $Ru_3(CO)_{12}$ with 4-methyl-2-pentyne gives Ia as one of several products.[13] The yield and purity of Ia can be optimized by modification of the reaction conditions previously reported for this compound (see Experimental Section).

The low-temperature limiting ^{1}H NMR spectrum of Ia is attained at −35 °C where three methyl resonances at δ 2.54, 2.23 and 1.9 are observed (relative intensity 1:1:1; Figure 1). Above this temperature, the two upfield resonances broaden, merge, and coalesce to a single resonance δ 2.04. The hydride resonance at δ −20.04 and the methyl resonance at δ 2.54 remain unchanged throughout the temperature range examined. With a coalescence temperature 265 K, the free energy of activation for this process is 56.0 ± 1 kJ/mol.[14] Due to the relatively low symmetry of this complex, it would appear that no single motion of the organic ligand nor any combination of just hydride and carbonyl migrations would average the methyl resonances. We then undertook an investigation of the variable-temperature ^{13}C NMR spectra of a ^{13}CO-enriched

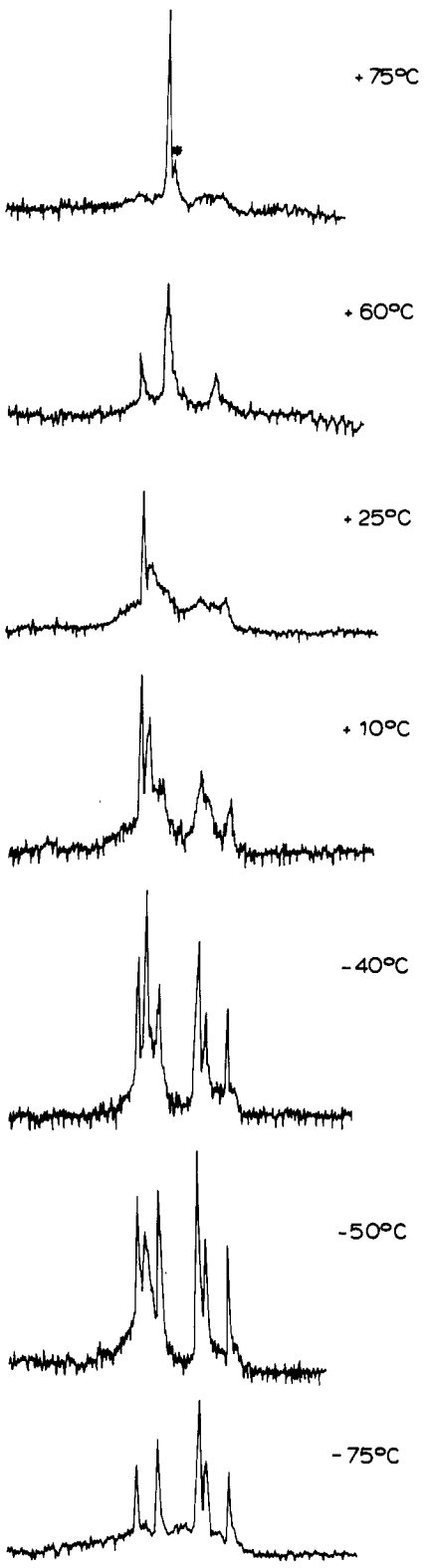


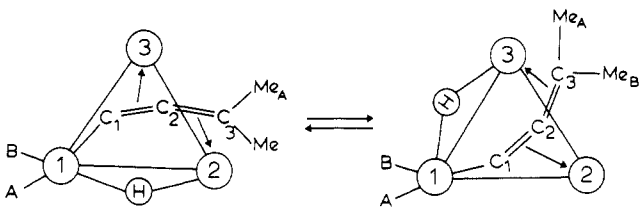
Figure 2. Variable-temperature ^{13}C NMR spectra of $HRu_3(CO)_9[CH_3C{=}C{=}C(CH_3)_2]$ in the carbonyl region. The * denotes an impurity due to an incipient decomposition of the compound.

(12) M. Castiglioni, L. Milone, D. Osella, G. A. Vaglio, and M. Walle, *Inorg. Chem.*, *15*, 394 (1976).

(13) S. Aime, L. Milone, E. Sappa, E. Rosenberg, A. M. Manotti Lanfredi, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 2023 (1981).

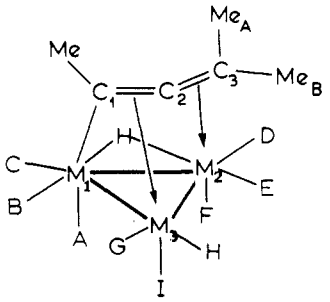
(14) Estimated from coalescence temperature (±1.0 K) using the equation $\Delta G_c^* = 4.57\ (T_c)\ (9.97 - \log T_c/\delta\nu)$: D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.* 656 (1971).

Scheme I



sample of Ia. At −75 °C five resonances are resolved in the carbonyl region at δ 197.9, 195.9, 192.0, 191.3, and 189.1 (relative intensity 1:1:2:1:1 (Figure 2). Nine resonances should be observed in the low-temperature limit according to the solid-state structure for a direct analogue of Ia,[15] but the limited solubility of Ia below −80 °C precluded going to lower temperature. As the temperature is increased to −50 °C, however, a new resonance appears at δ 197.2 (relative intensity 3). Thus, at −50 °C, we can account for nine carbonyl groups. This resonance continues to sharpen as the temperature is increased. At +10 °C all the resonances except the resonance at δ 197.9 (relative intensity 1) are beginning to broaden. The resonance at δ 197.9 remains sharp to +25 °C. At this temperature, a new broadened resonance at δ 190.2 appears which is the weighted average of the resonances at δ 191.3 and 189.1. As the temperature is raised to +60 °C, a single resonance of relative intensity 6 is observed at δ 195.3, which is the weighted average of all resonances except the ones at δ 197.9 and 190.2, which are only slightly broadened. Above this temperature, the resonance at δ 195.3 continues to sharpen while the resonances at δ 197.9 and 190.2 collapse into the base line. At −75 °C only the resonances at δ 192.0 and 189.1 show coupling to the hydride (8 and 10 Hz, respectively) indicating trans H–M–CO relationship.[2] One of the two resonances at δ 192.0 remains as a singlet in the ^{1}H-coupled spectrum showing that the decoupled resonance of relative intensity 2 at this frequency is actually the superposition of two magnetically inequivalent resonances, only one of which is coupled to the hydride.

We can interpret the changes in the ^{13}C NMR spectra of Ia with temperature and assign almost all the resonances unambiguously by considering the multistage exchange process using the labeling scheme for Ia. The first stage



Ia, M = Ru
Ib, M = Os

of the process involves axial–radial exchange at Ru(3), CO(G), CO(H), and CO(I) which gives rise to the resonance of relative intensity 3 at δ 197.2. We have recently shown that the barriers to axial–radial carbonyl site exchange in $HM_3(CO)_9L$ (L = 5-electron donor organic ligand) (M = Ru, Os) are considerably lower at the metal atoms not bridged by the hydride.[3,4,16,17] The second stage of the process results in the averaging of the carbonyl groups at Ru(3) with three other carbonyls and in the simultaneous averaging of the two carbonyl resonances at δ 191.3 and 189.1 with each other. It is in this temperature range that the two methyls are also averaged in the ^{1}H NMR spectra. An exchange process which averages the carbonyl groups on Ru(3) with those on Ru(2) CO(D), CO(E), and CO(F) while averaging the two radial carbonyls on Ru(1) (CO(B) and C)(C) and the two methyl groups on C(3) of the organic ligand is shown in Scheme I. This involves "edge hopping" of the hydride from the Ru(1)–Ru(2) to Ru(1)–Ru(3) edge which appears to be concerted with a wagging motion of the organic ligand pivoting on C(2). We, of course, cannot be certain that the hydride migration does not directly preceed or follow the required wagging motion but both processes are necessary to explain the observed changes in the ^{13}C and ^{1}H NMR spectra. This process averages the two radial carbonyls on Ru(1) with each other but not with the axial carbonyl on Ru(1) (CO(A)). On this basis, we can assign the resonance at δ 197.9 to the axial carbonyl and the resonances at δ 191.3 and 189.1 to the radial carbonyls on Ru(1). Opening of the hydride bridge at Ru(2) only in this stage of the exchange allows for averaging of the axial and radial carbonyls at the ruthenium atoms as is observed. We have recently shown, by kinetic deuterium isotope effect studies, that opening of the hydride bridge is directly linked to axial–radial exchange of carbonyl groups in this type of complex.[16b] At the upper end of the temperature range examined, the axial and radial carbonyl groups on Ru(1) also begin to average and this process requires opening of the hydride bridge at Ru(1) as well. In the lower energy exchange process which averages the radial carbonyl groups with each other but not with axial carbonyl, no motion of the carbonyl groups is required. We cannot discern whether hydride bridge opening is actually necessary for averaging the CO groups on Ru(1). If it is, however, it seems reasonable that hydride migration around the cluster if taking place since alternate opening of the bridge at Ru(2) and then at Ru(1) (or Ru(3) and then Ru(1)) is not compatible with the fact that the edge hopping of the hydride from the Ru(2)–Ru(1) edge to the Ru(3)–Ru(1) edge is much faster than the alternate opening of the bridge on a single edge of the cluster.

We have also been able to synthesize the osmium analogue of Ia by reaction of $H_2Os_3(CO)_{10}$ with 4-methyl-2-pentyne (see Experimental Section). Unlike the ruthenium analogue, Ib shows three sharp methyl resonances in the room-temperature ^{1}H NMR spectrum at δ 2.37, 2.08 and 1.79 (Figure 1) and a hydride resonance at δ −19.95. As the temperature is increased to +90 °C, the two high-field methyl resonances broaden and then merge to a single peak; with a coalescence temperature 373 K, the free energy of activation for this process is 80.6 ± 1 kJ/mol. We then went on to record the VT ^{13}C NMR spectra of an enriched sample of Ib. In the low-temperature limiting spectrum at −90 °C all nine carbonyl resonances can be accounted for at δ 206.5, 204.9, 202.7, 201.5, 200.2, 197.5, and 196.3 (relative intensity 1:1:1:3:1:1:1; Figure 3). At −70 °C the resonances at δ 206.5 and 202.7 are noticeably broadened, and by −52 °C a new resonance has appeared at δ 203.1 (relative intensity 3) which is the weighted average of the resonances at δ 206.5 and 202.7 and one of the

(15) G. Gervasio, D. Osella, and M. Valle, *Inorg. Chem.*, **15**, 1221 (1976).

(16) (a) S. Aime, O. Gambino, L. Milone, E. Sappa, and E. Rosenberg, *Inorg. Chim. Acta*, **15**, 53 (1975). (b) E. Rosenberg, C. B. Thorsen, S. Aime, L. Milone, *J. Organometal. Chem.* submitted for publication.

(17) S. Aime, L. Milone, D. Osella, M. Valle, and E. W. Randall, *Inorg. Chim. Acta*, **20**, 217 (1976).

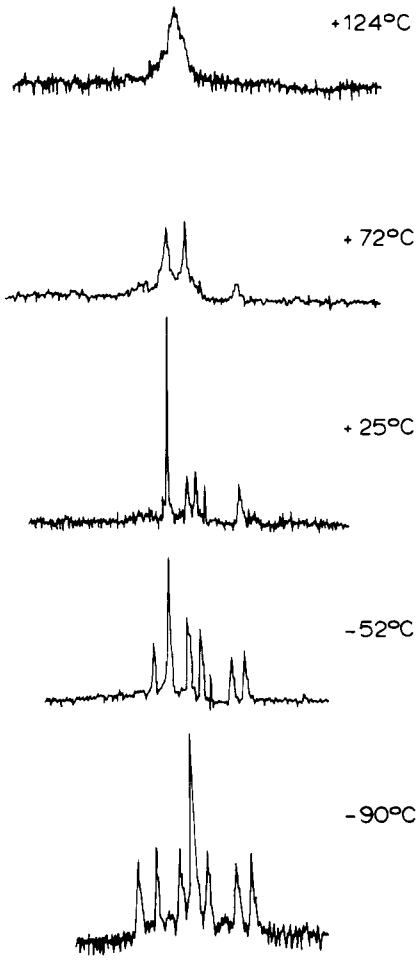


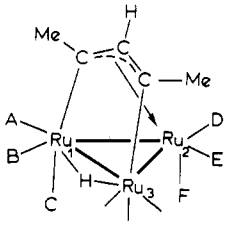
Figure 3. Variable-temperature ^{13}C NMR spectra of $HOs_3(CO)_9[CH_3C{=}C{=}C(CH_3)_2]$ in the carbonyl region.

apparently overlapping resonances of relative intensity 3 at δ 201.5. At +25 °C the resonances at δ 204.9 and 197.5 and one of the two overlapping resonances at δ 201.5 have broadened considerably, leaving three relatively sharp resonances of relative intensity 1 at δ 201.5, 200.2, and 196.3 and a sharp resonance of relative intensity 3 at δ 203.1. As the temperature is increased further the resonance at δ 203.1 remains sharp while a new peak emerges at δ 201.3 which masks the resonances at δ 201.5 and 200.2. The resonance at δ 196.3 is somewhat broadened above +72 °C. Above this temperature, this resonance continues to broaden and the two more intense resonances also begin to broaden and coalesce at approximately 124 °C. Only the resonances at δ 197.5 and 196.3 show coupling to the hydride (about 10 Hz), indicating a trans relationship to the hydride.

The changes in the variable-temperature ^{13}C NMR spectra can be understood in terms of a similar mechanism to that of the ruthenium analogue but where the barriers and the order of the various stages of the exchange process are somewhat different. These exchange processes are discussed in terms of the same labeling scheme used for Ia. The first stage of the exchange involves axial-radial exchange of carbonyl groups on Os(3) CO(G) and Co(H) CO(I) as in the ruthenium analogue. Here, however, the barrier is slightly higher, and the low-temperature limiting spectrum is observed before the compound becomes too insoluble. We have previously observed that the barrier to axial–radial carbonyl exchange is slightly higher at nonbridged osmium atoms than at nonbridged ruthenium atoms in other $HM_3(CO)_9(L)$ (L = $C{\equiv}CC(CH_3)_3$ compounds.[16] The second stage of the exchange process in Ib averages the carbonyl groups at (Os(2) CO(D), CO(E), and CO(F) without simultaneously averaging the radial carbonyls at Os(1) (CO(B) and CO(C)) as in the ruthenium analogue. This suggests that opening of the hydride bridge at Os(2) is occurring to allow averaging of the carbonyl groups on Os(2). We cannot discern whether the opening of the bridge at Os(2) is followed by edge hopping of the hydride. We do know, however, that the methyl groups on C(3) of the ligand are magnetically inequivalent in the same temperature range. At higher temperatures unfortunately, we only observe the progressive broadening of CO(C) and cannot tell if CO(A) remains sharp while CO(B) broadens, as in the ruthenium case, since both CO(A) and CO(B) are masked by the emerging resonance which is the average of the carbonyl groups of Os(2). The higher temperatures necessary to bring about the averaging of the carbonyl groups on Os(1) compared with Ru(1) apparently results in the overlap of this process with a higher energy process which results in the averaging of all the carbonyl groups. This could be brought about by intermetallic scrambling or by simultaneous rotation of the organic ligand and hydride migration around the metal triangle. We can conclude from these results that the barrier to the motion of the organic ligand is higher for osmium than for ruthenium. We cannot say at this time whether edge hopping of the hydride is directly coupled with wagging of the organic ligand in these systems. Our recent observations of deuterium isotope effects in hydride migrations[16b] holds out the possibility of observing such an effect on the averaging of the inequivalent methyl groups on C(3) of the ligand. The synthesis of the deuterated analogue and a study of their ^1H and ^{13}C NMR is under way.

(B) "Allylic" Derivatives. Our previous dynamic NMR work on the "allylic" derivatives of type II was confined to an examination of the low-temperature range (−90 to +25 °C).[17] We now report the high-temperature ^{13}C NMR of the symmetrical "allylic" complex $HRu_3(CO)_9(CH_3CCHCCH_3)$ (II) and of its monophosphine derivative $HRu_3(CO)_8(CH_3CCHCCH_3)P(C_6H_5)_3$ (III) in order to compare their high-temperature behavior with Ia.

The ^{13}C NMR spectrum of II at +25 °C consists of one sharp resonance at δ 197.7 which is the average of the carbonyl groups on Ru(2) CO(D), CO(E), and CO(F) (relative intensity 3) and of these three broadened resonances at δ 195.9, 192.3, and 190.4 (relative intensity 2:2:2).

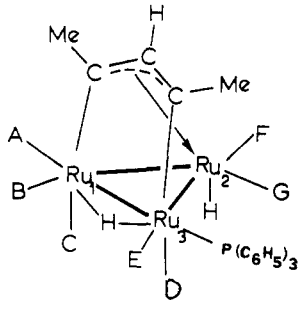


II

As the temperature is increased, these resonances average to a single resonance at δ 192.9 at +78 °C. This is the result of localized exchange of CO(A), CO(B), and CO(C) at Ru(1) and Ru(3). As the temperature is increased further, this resonance (relative intensity 6) continues to sharpen and then begins to broaden along with the resonance at δ 197.7. The averaging of the resonances of the carbonyl groups at Ru(1) and Ru(3) arises from either alternate opening or even stretching of the hydride bridge or by migration of the hydride around the metal triangle.[16b] For the "allenic" structure Ia it is clear that

hydride edge hopping is a lower energy process than hydride migration around the ring. In the case of II, however, we can only say that within the temperature range examined the organic ligand is not moving and localized axial–radial exchange, which appears to require opening of the hydride bridge,[16b] is independent of any motion of the organic ligand. We cannot say whether the opening of the hydride bridge then results in actual hydride migration. The highest energy process of which only the initial stages are observed at +122 °C must involve either intermetallic CO scrambling or a combined rotation of the organic ligand and hydride migration around the triangle.

The phosphine derivative of II, III, has been previously



III

reported[18] and its structure elucidated by ^{1}H NMR spectroscopy. The low-temperature limiting ^{13}C NMR spectrum of a sample of III at −87 °C shows seven resonances at 209.8, 201.9, 197.5, 195.2 (J(C,H) = 12.0 Hz), 194.5, 193.4, and 191.8 ppm (J(C,P) = 7.5 Hz, J(C,H) = 14.0 Hz, relative intensity 1:1:1:1:2:1:1). As the temperature is increased to −50 °C, the resonances at 209.8 and 194.5 ppm broaden, coalesce, and emerge as a single resonance of relative intensity 3. This corresponds to the axial–radial averaging process of the carbonyl groups on Ru(2) in II. As the temperature is increased to room temperature, no noticeable broadening of the remaining five resonances is observed. A further increase in the temperature to +50 °C did reveal some broadening of these resonances at 197.5, 193.4, and 191.8 ppm, but at this temperature the analogous carbonyl resonances due to the carbonyl groups on Ru(1) and Ru(3) in II were already coalesced. Above +65 °C III began to decompose. The dynamic behavior of the carbonyl groups in II and III are thus very similar except that phosphine substitution appears to raise the barrier for axial–radial exchange at the hydride-bridged Ru atoms. It is doubtful that this increased barrier is steric in origin since we have shown that phosphine substitution at a non-bridged Ru atom in $HRu_3(CO)_8(C{\equiv}CC(CH_3)_3)P(C_6H_5)_3$ does not effect the barrier to axial–radial exchange.[18] Since we do observe a noticeable effect here, it seems reasonable that the increased barrier to axial–radial exchange is due to an increased metal–hydrogen bond strength.[19]

Experimental Section

Synthesis of Compound Ia. A solution of $[Ru_3(CO)_{12}]$ (0.500 g) and $H_3CC{\equiv}CCH(CH_3)_2$ (0.3 mL) in cyclohexane (100 mL) was heated under reflux under N_2 for 1 h. After the solution was cooled, the unreacted $[Ru_3(CO)_{12}]$ was recovered by filtration of the reaction mixture. Chromatography of the filtrate (TLC, SiO_2; eluant, light petroleum) gave Ia with other products. Successive purification by TLC and crystallization were necessary in order to get Ia in sufficient purity (ca. 0.050 g, 10%). (See ref 13 for spectroscopic and analytical data).

Synthesis of Compound Ib. A solution of $H_2Os_3(CO)_{10}$ (0.450 g) and $H_3CC{\equiv}CCH(CH_3)_2$ in hexane (50 cm^3) was allowed to stand for 1 day at room temperature. Removal of solvent and TLC (SiO_2; eluant, toluene) gave $[Os_3(CO)_{10}(H_3C{\equiv}CCH(CH_3)_2]$ (0.300 g): mass spectrum, m/e (M^+) 938; IR (CO stretch (n-hexane)) 2099 (w), 2053 (vs), 2041 (w), 2027 (s), 2007 (m), 1998, 1846 (w, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.55 (s, 3), 2.27 (sept 1, J_{HH} = 6.0 Hz), 0.97 (Cl, 6, J_{HH} = 6.0 Hz). When this compound was heated in n-heptane at reflux for 2 h, compound Ib is obtained in almost quantitative yield: mass spectrum, m/e (M^+) 910 followed by loss of nine CO; IR (CO stretch (n-hexane)) 2094 (m), 2066 (s), 2041 (vs), 2021 (vs), 2008 (s), 1997 (s), 1989 (m), 1984 (w), 1974 (w) cm^{-1}.

$[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ were enriched by stirring for 4 days in sealed ampules, at +50 and +110 °C, respectively, in the presence of <1 atm of 90% enriched ^{13}CO (Monsanto).

^{1}H NMR spectra were recorded on a JEOL 60 H1 spectrophotometer and ^{13}C NMR spectra on a JEOL PFT-100 spectrometer in the Fourier transform mode. The chemical shifts are downfield positive with respect to internal Me_4Si. The solvents ($CDCl_3$, CD_2Cl_2, and $C_6D_5CD_3$) were purchased from C.E.A. and used immediately after being dried over molecular sieves. $Cr(acac)_3$ (0.05 M) was used as a relaxation reagent for CO groups.

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Registry No. Ia, 80400-37-9; Ib, 80662-58-4; II, 56943-13-6; III, 72708-35-1; $Ru_3(CO)_{12}$, 15243-33-1; $H_2Os_3(CO)_{10}$, 41766-80-7.

(18) C. Jangala, E. Rosenberg, D. Skinner, S. Aime, L. Milone, and E. Sappa, *Inorg. Chem.*, 19, 1571 (1980).

(19) Phosphine substitution on a hydride-bridged metal atom has been shown to quench the acidity of the metal hydrogen bond (see ref 2 for examples), and we have observed this for $HM_3(CO)_9L$ (L = $C{\equiv}CC(CH_3)_3$).