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Contribution from the Department of Chemistry,
University of Illinois, Urbana, Illinois 61801

Solution Structures and Dynamics of Complexes of $H_2Os_3(CO)_{10}$ with Lewis Bases

JEROME B. KEISTER*[1] and JOHN R. SHAPLEY

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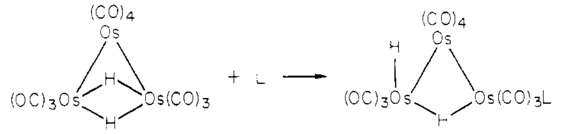
The unsaturated cluster $H_2Os_3(CO)_{10}$ reacts with a variety of Lewis bases L, including carbon monoxide, phosphines, phosphites, arsines, stibines, amines, nitriles, isocyanides, halides, and pseudohalides, to form 1:1 adducts $H_2Os_3(CO)_{10}L$. Each of these adducts has been shown to contain one axial, terminal hydride ligand and one bridging hydride ligand. Variable-temperature ^1H and ^{13}C NMR studies reveal that the two hydride ligands and two carbonyl ligands undergo simultaneous fluxional exchange. A turnstile-like mechanism is proposed. Variation of the free energy of activation for the exchange process with the steric and electronic properties of L suggests that the transition state involves two equivalent hydride ligands bridging the same metal-metal vector.

Introduction

The unsaturated cluster $H_2Os_3(CO)_{10}$ behaves in many respects as a transition-metal analogue of diborane. This unique cluster has been shown to transfer hydride ligands to unsaturated molecules such as olefins,[2] acetylenes,[3] and isocyanides.[4,5] The first interaction of each of these substrates with the cluster is very likely to be formation of a Lewis acid-base adduct. Simple Lewis bases L, including phosphines, phosphites, arsines, stibines, carbon monoxide, alkyl and aryl isocyanides, nitriles, amines, halides, and pseudohalides, react with $H_2Os_3(CO)_{10}$ upon mixing to give isolable 1:1 adducts $H_2Os_3(CO)_{10}L$ (eq 1).[6] On the basis of spectroscopic studies,



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each of these adducts was proposed to contain one bridging and one terminal hydride ligand.[7,8] X-ray crystallographic studies have confirmed this proposal for solid-state structures by direct location of the hydride ligands in $H_2Os_3(CO)_{10}(PPh_3)$[9] and by inference from the arrangements of the nonhydrogen ligands in $H_2Os_3(CO)_{11}$[10] and $H_2Os_3(CO)_{10}(t\text{-}BuNC)$.[11]

The ^1H NMR spectra of the adducts $H_2Os_3(CO)_{10}L$ showed evidence for intramolecular bridge-terminal hydride exchange.[7,8] Two limiting cases are possible for the transition state that occurs during this exchange, namely, one with both hydride ligands in terminal positions or one with both hydrides bridging. Since $H_2Os_3(CO)_{11}$ is a probable intermediate in the formation of $H_2Os_3(CO)_{10}$ from $Os_3(CO)_{12}$,[12] we felt that the transition state for bridge-terminal hydride exchange (in which both hydrides are equivalent) might be related to the transition state for the dihydrogen activation (oxidative addition) involved in the formation of $H_2Os_3(CO)_{11}$. To learn more about the transition state for bridge-terminal hydride exchange in $H_2Os_3(CO)_{10}L$, we have determined the influence of the base L upon the barrier to exchange for several sets of bases with differing electronic and steric properties. In addition we have examined the ^{13}C NMR spectra of representative ^{13}CO-enriched adducts in order to more fully define the structures adopted in solution as well as their dynamics. Recently, Aime, Osella, Milone, and Rosenberg[13] reported variable-temperature ^{13}C NMR spectra of $H_2Os_3(CO)_{10}L$ (L = PPh_3, $P(i\text{-}Pr)_3$, and $P(O\text{-}i\text{-}Pr)_3$), which showed that hydride exchange is accompanied by exchange of two carbonyl ligands. These results agree with our studies, which in addition provide information for a more detailed picture of the fluxional process.

Results and Discussion

Synthesis and Characterization of $H_2Os_3(CO)_{10}L$. Upon the addition of each of a variety of Lewis bases, including carbon monoxide, phosphines, phosphites, arsines, stibines, isocyanides, nitriles, pyridines, amines, halides, and pseudohalides, the purple solution of $H_2Os_3(CO)_{10}$ in an inert solvent rapidly turns yellow. Removal of the solvent in most cases gives the complex $H_2Os_3(CO)_{10}L$ in essentially quantitative yield. Characterizations of adducts with L = CO,[7,8] PPh_3,[7,8] PMe_2Ph,[7,8] CN-t-Bu,[4,5] CNMe,[4,5] and PhCN[7] have already been reported. Syntheses of adducts with L = $P(c\text{-}C_6H_{11})_3$, $AsPh_3$, $AsMe_2Ph$, and $P(OMe)_3$ are described in the Experimental Section. Many other adducts have been prepared and characterized spectroscopically in solution. Included as supplementary data is a complete listing of the ν_{CO} IR data (Table A) obtained for all adducts prepared, together with the solid-state IR spectra (Figure X) of $H_2Os_3(CO)_{11}$ and $D_2Os_3(CO)_{11}$.

The existence of one bridging and one terminal hydride in each of these adducts was originally postulated because of the extremely large chemical shift difference between the two hydride NMR resonances. At low temperatures in each case (see Table I; additional compounds are included as supple-

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(1) Present address: Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214.

(2) (a) J. B. Keister and J. R. Shapley, *J. Organomet. Chem.*, **85**, C29 (1975); (b) J. B. Keister and J. R. Shapley, *J. Am. Chem. Soc.* **98**, 1056 (1976).

(3) (a) W. G. Jackson, B. F. G. Johnson, J. W. Kelland, J. Lewis, and K. T. Schorpp, *J. Organomet. Chem.*, **87**, C27 (1975); (b) M. Tachikawa, J. R. Shapley, and C. G. Pierpont, *J. Am. Chem. Soc.*, **97**, 7172 (1975); (c) A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1614 (1975); (d) M. Laing, P. Sommerville, Z. Dawoodi, M. J. Mays, and P. J. Wheatley, *J. Chem. Soc., Chem. Commun.*, 1035 (1978).

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(6) The conventional line connecting metal atoms bridged by a hydride ligand has been omitted from our structural representations in accordance with the suggestion of H. D. Kaesz (see Y. C. Lin, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, **103**, 1216 (1981), and references therein). The coordination around each of the bridged osmium atoms is octahedral if the direct metal-metal bond is omitted. However, the M-H-M interaction should be considered a three-center, two-electron bond.

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Table I. ^1H NMR Spectra for $H_2Os_3(CO)_{10}L$

L	Hydride Resonances, τ	coupling, Hz	$\Delta G^{\ddagger}$, kcal/mol[i]	T, K
CO[a]	(a) 20.25 (d), (b) 29.96 (d)	J(ab) = 3.8	12.9	240
PPh_3[a]	(a) 20.14 (d), (b) 29.71 (dd)	J(ab) = 4.0, J(bP) = 11.0	12.5	236
$PMePh_2$[b,d]	(a) 20.28 (d), (b) 30.08 (dd)	J(ab) = 3.5, J(bP) = 9.5	11.8	229
PMe_2Ph[a,e]	(a) 20.58 (d), (b) 30.43 (dd)	J(ab) = 4.0, J(bP) = 12.0	11.2	212
PMe_3[a]	(a) 20.56 (d), (b) 30.75 (dd)	J(ab) = 3.8, J(bP) = 12.5	11.3	216
PEt_3[b]	(a) 20.44 (d), (b) 30.91 (dd)	J(ab) = 3.8, J(bP) = 12.0	12.0	228
PBu_3[b]	(a) 20.51 (d), (b) 30.92 (dd)	J(ab) = 3.6, J(bP) = 11.0	12.0	227
$P(c\text{-}C_6H_{11})_3$[b]	(a) 20.04 (d), (b) 30.52 (dd)	J(ab) = 3.4, J(bP) = 9.5	13.6	258
$P(OMe)_3$[a,f]	(a) 20.36 (d), (b) 30.67 (dd)	J(ab) = 4.0, J(bP) = 12.0	12.3	241
$P(OEt)_3$[a]	(a) 20.35 (d), (b) 30.61 (dd)	J(ab) = 4.0, J(bP) = 11.9	12.3	233
$P(O\text{-}i\text{-}Pr)_3$[a]	(a) 20.29 (dd), (b) 30.48 (dd)	J(ab) = 4.0, J(bP) = 11.0, J(aP) = 0.9	12.8	246
$P(OPh)_3$[a]	(a) 20.38 (dd), (b) 30.42 (dd)	J(ab) = 3.8, J(bP) = 12.9, J(aP) = 1.3	13.1	254
$P(OCH_2)_3CC_2H_5$[a]	(a) 20.46 (d), (b) 30.45 (dd)	J(ab) = 4.0, J(bP) = 12.1	12.5	242
$AsPh_3$[a]	(a) 20.21 (d), (b) 29.92 (d)	J(ab) = 4.0	11.9	224
$AsMe_2Ph$[a]	(a) 20.48 (d), (b) 30.44 (d)	J(ab) = 4.0	11.0	226
$SbPh_3$[a]	(a) 20.26 (d), (b) 30.28 (d)	J(ab) = 3.8	11.5	225
$CNMe$[b,g]	(a) 20.07 (d), (b) 29.81 (d), (c) 20.01 (d), (d) 29.75 (d) (ab/cd = 3)	J(ab) = 4.1 J(cd) = 3.9	13.3 13.7	257
$CN\text{-}t\text{-}Bu$[b,h]	(a) 20.09 (d), (b) 29.85 (d), (c) 19.94 (d), (d) 29.74 (d) (ab/cd = 2.7)	J(ab) = 4.0 J(cd) = 3.8	12.8 13.2	259
$4\text{-}NC_5H_4Me$[a]	(a) 19.47 (d), (b) 25.30 (d), (c) 19.81 (d), (d) 25.69 (d) (ab/cd = 3)	J(ab) = 3.6 J(cd) = 4.0	13.4 13.0	246
$4\text{-}NC_5H_4Br$[a]	(a) 19.44 (d), (b) 25.23 (d), (c) 19.74 (d), (d) 25.69 (d) (ab/cd = 2.9)	J(ab) = 3.8 J(cd) = 4.1	13.2 12.8	253
$I^-(K^+)$[c]	(a) 19.14 (d), (b) 28.78 (d)	J(ab) = 4.2	11.5	227
$Br^-(K^+)$[c]	(a) 19.49 (d), (b) 27.18 (d)	J(ab) = 4.2	11.9	232
$Cl^-(Li^+)$[c]	(a) 19.76 (d), (b) 26.30 (d)	J(ab) = 4.4	12.2	243

[a] In dichloromethane. [b] In deuteriochloroform. [c] In acetone. [d] Other signals: τ 7.29 (d, 3 H, J(PH) = 11.0 Hz), 2.44 (m, 10 H). [e] Other signals: τ 8.58 (d, 6 H, J(PH) = 10.0 Hz), 2.4 (m, 5 H). [f] Other signals: τ 6.24 (d, 9 H, J(PH) = 12.0 Hz). [g] Other signals: τ 6.22 (s, 3 H). [h] Other signals: τ 8.55 (s, 9 H). [i] Estimated error limits are ±0.2 kcal/mol.

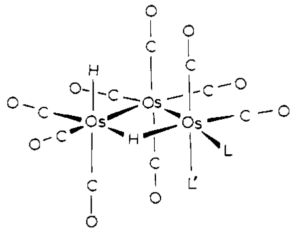

Figure 1. Configuration adopted by $H_2Os_3(CO)_{10}(PR_3)$ (L = PR_3, L′ = CO), based upon the X-ray crystal structure of $H_2Os_3(CO)_{10}(PPh_3)$, and by $H_2Os_3(CO)_{10}(CNR)$ (L = CO, L′ = CNR) in the solid state, based upon the X-ray crystal structure of $H_2Os_3(CO)_{10}(CN\text{-}t\text{-}Bu)$.

mentary data in Table B) one hydride resonance is observed near τ 20 and a second of equal intensity between τ 26 and 30, with a coupling constant of 4 Hz between the two signals. On the basis of similarities with chemical shifts observed for other osmium hydride complexes,[14] the lower field resonance is assigned to a terminal hydride and the higher field resonance to a bridging hydride ligand; with phosphorus donor ligands, a much larger coupling constant is noted for the higher field resonance (ca. 12 Hz) than for the lower field signal (less than 2 Hz). This is consistent with the solid-state structure found for $H_2Os_3(CO)_{10}(PPh_3)$ (Figure 1, L = PPh_3, L′ = CO), in which the phosphine ligand occupies the equatorial coordination site cis to the bridging hydride ligand.[10] On the other hand, the isocyanide ligand of $H_2Os_3(CO)_{10}(CN\text{-}t\text{-}Bu)$[11] is found to be axially coordinated and to be on the opposite side of the Os_3 plane from the axial, terminal hydride (Figure 1, L = CO, L′ = CN-*t*-Bu). However, the static ^1H NMR spectra of $H_2Os_3(CO)_{10}(CNR)$ (R = Me, *t*-Bu) indicate that two isomers of unequal populations exist in solution, each isomer having a single hydride resonance at ca. τ 20 and a second at ca. τ 30 with a coupling constant of 4 Hz between the two resonances. These two isomers are easily accounted for by the two possible relative orientations of the axial hydride and axial isocyanide ligands; the second isomer must have these two ligands on the same side of the Os_3 plane. Other complexes displaying ^1H NMR spectra similar to those for the adducts with alkyl isocyanides include $H_2Os_3(CO)_{10}L$, L = $4\text{-}NC_5H_4Me$, $4\text{-}NC_5H_4Br$, N_3^-, and CN^-; the inference is that L in each of these adducts is coordinated in the same axial site as was found for L = CN-*t*-Bu.

Hydride Fluxionality. Temperature-dependent ^1H NMR spectra are observed for all adducts $H_2Os_3(CO)_{10}L$ due to a fluxional process that interchanges the hydride ligand environments. As the temperature of the sample is raised, in each case the hydride resonances observed in the limiting slow-exchange spectrum broaden and collapse into the base line. For $H_2Os_3(CO)_{10}(PMe_2Ph)$ at 50 °C the broad ($\Delta\nu_{1/2}$ 25 Hz), coalesced resonance is observed at τ 25.36. However, in all cases decomposition occurs before the limiting fast-exchange spectra can be obtained. In the presence of excess ligand L (L = PMe_2Ph, $AsMe_2Ph$, CNMe, $4\text{-}NC_5H_5Me$, and others) separate ^1H NMR resonances for free and coordinated ligands can be observed at temperatures at which the hydride resonances are in the intermediate-exchange region. This observation, in addition to the presence of ^{31}P–^{13}C coupling in the fast-exchange ^{13}C NMR spectra of $H_2Os_3(CO)_{10}L$ (L = PPh_3, PMe_2Ph) (vide infra), rules out ligand dissociation as a mechanism for hydride exchange.

The free energy of activation for hydride interchange in $H_2Os_3(CO)_{10}L$ can be estimated in each case from temperature-dependent line broadening near the slow-exchange limit. The values of $\Delta G^{\ddagger}$ are found to vary between 13.5 and 11.2 kcal/mol, depending upon the steric and electronic properties of L (vide infra). For $H_2Os_3(CO)_{10}(PMe_2Ph)$ the value of 11.2 kcal/mol obtained from line broadening near the slow-

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(14) For comparison, the terminal hydride resonances of $H_2Os(CO)_4$ and $H_2Os_2(CO)_8$ are observed at τ 18.73 and 20.11, respectively, while bridging hydride resonances generally are found above τ 25 (e.g., $HOs_3(\mu\text{-}SC_2H_5)(CO)_{10}$, τ 27.5).[15]

(15) (a) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972); (b) E. Muetterties, Ed., "Transition Metal Hydrides", Marcel Dekker, New York, 1971, and references therein.

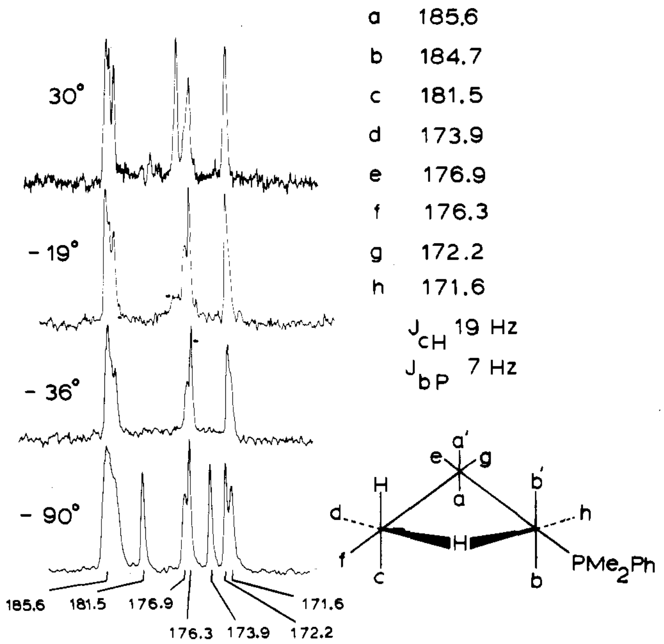

Figure 2. ^{13}C NMR spectra of ca. 40% ^{13}CO-enriched $H_2Os_3(CO)_{10}(PMe_2Ph)$ in acetone-d_6 at various temperatures.

exchange limit agrees well with the estimate of 11.4 kcal/mol obtained from line narrowing of the coalesced resonance.

Carbonyl Fluxionality of $H_2Os_3(CO)_{10}(PMe_2Ph)$. A description of the variable-temperature behavior of $H_2Os_3(CO)_{10}(PMe_2Ph)$ is typical of the phosphorus donor adducts. The limiting slow-exchange ^{13}C NMR spectrum of $H_2Os_3(CO)_{10}(PMe_2Ph)$ at -90 °C in deuterioacetone displays six single-carbonyl resonances and one broad signal due to four overlapping carbonyl resonances (Figure 2). The spectrum is consistent with structure established for the PPh_3 adduct (Figure 1). The five lowest field resonances are assigned to the five axial carbonyls by comparison to the chemical shifts of axial carbonyls in other triosmium clusters,[16] and the five resonances to higher field are assigned to the equatorial carbonyls. The axial resonance at 181.5 ppm is strongly coupled to the terminal hydride (J = 19 Hz). Since no other $^{13}C-^{1}H$ couplings are resolvable, this resonance is assigned to the unique axial carbonyl trans to the terminal hydride. The broad signal of weight 4 is then assigned to the other two axial carbonyl pairs. The equatorial carbonyl resonances at 176.9 (1 C) and 171.6 (1 C) ppm are broad in the $^{13}C\{^{1}H\}$ NMR spectrum; this broadening is presumed to be due to unresolved coupling to the ^{31}P nucleus. The 176.9-ppm resonance is assigned to the equatorial carbonyl on the $Os(CO)_4$ unit that is located trans to the phosphine ligand through the metal-metal bond;[17] this chemical shift is similar to equatorial carbonyls on other unsubstituted triosmium clusters. The resonances at 176.3, 173.9, and 171.6 ppm are slightly broadened in the ^{1}H-coupled spectrum. Since the 171.6-ppm signal is also coupled to the ^{31}P nucleus, it is assigned to the equatorial carbonyl cis to the phosphine ligand and trans to the bridging hydride. The other two resonances, 176.3 and 173.9 ppm, are then assigned to equatorial carbonyls cis to the terminal hydride. On the basis of these assignments, it is suggested that a hydride ligand causes upfield shifts for carbonyls coordinated to the same metal center.

As the temperature is raised from -90 °C, the ^{13}C NMR spectrum of $H_2Os_3(CO)_{10}(PMe_2Ph)$ undergoes changes due to exchange of the resonances at 181.5 and 173.9 ppm (Figure 2). At -36 °C these two signals have collapsed into the base line. At -19 °C a broad, coalesced resonance appears at 177.3 ppm. This resonance sharpens at +30 °C to a single peak corresponding to two carbonyls. At -19 °C the other four axial carbonyls are resolved into a singlet at 185.3 ppm of weight 2 and a doublet at 184.7 ppm of weight 2 with coupling to ^{31}P of 7 Hz.[18] The appearances of the resonances due to the axial carbonyl pairs suggest that the fluxional process exchanging the 181.5- and 173.9-ppm signals also generates an effective plane of symmetry coincident with the triosmium plane. At 30 °C the resonances which appear at 172.2 and 171.6 ppm at -90 °C occur as a single peak at 171.8 ppm, but this is due to accidently overlapping resonances, rather than fluxionally averaged resonances, because the chemical shifts of these signals move together as the temperature is raised. If -19 °C is taken as the coalescence temperature of the 181.5- and 173.9-ppm signals, the free energy of activation at this temperature is estimated to be 12.0 kcal/mol. However, since the actual coalescence temperature is somewhat lower, this value agrees within experimental error with numbers obtained from the ^{1}H NMR spectra and suggests that the same process is responsible for both hydride and carbonyl fluxionality.

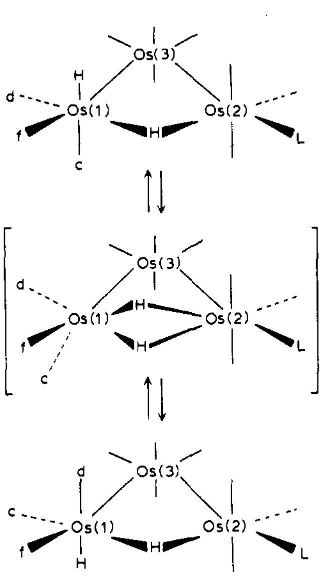

Figure 3. Proposed fluxional process for the complexes $H_2Os_3(CO)_{10}L$, where L occupies an equatorial position.

The mechanism shown in Figure 3 fully accounts for the observed ^{13}C and ^{1}H NMR behavior of $H_2Os_3(CO)_{10}(PMe_2Ph)$. Aime, Osella, Milone, and Rosenberg[13] were led to the same conclusion from their ^{13}C NMR study of the PPh_3, $P(i\text{-}Pr)_3$, and $P(O\text{-}i\text{-}Pr)_3$ adducts. A turnstile-like movement of the axial and bridging hydrides and axial and equatorial carbonyls about the Os-CO(f) axis results in simultaneous averaging of the environments of the two hydrides and the two carbonyls. It is not possible to distinguish which of the two equatorial carbonyls cis to the axial hydride is involved in the exchange, but the carbonyl trans to the bridging hydride is the most esthetically pleasing choice. For phosphines and other Lewis bases that give rise to equatorial coordination the turnstile process generates a transition state with a plane of symmetry bisecting the H-Os-H and OC(d)-Os-CO(c) angles and containing the triosmium plane, averaging the axial carbonyls on the other two metal atoms in the fast-exchange limit.

Carbonyl Fluxionality of $H_2Os_3(CO)_{10}L$ (L = CNMe and CN-*t*-Bu). The adducts $H_2Os_3(CO)_{10}(CNR)$ display two sets

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[16] For example, B. F. G. Johnson, J. Lewis, B. E. Reichert, and K. T. Schorpp, *J. Chem. Soc., Dalton Trans.*, 1403 (1976).

[17] Coupling to ^{31}P through a metal-metal bond can be quite large: G. F. Stuntz and J. R. Shapley, *J. Am. Chem. Soc.*, **99**, 607 (1977).

[18] The coupling constant between an equatorial ^{31}P nucleus and the axial carbonyls of $Os_3(CO)_9(PEt_3)_3$ is 7 Hz.[16]

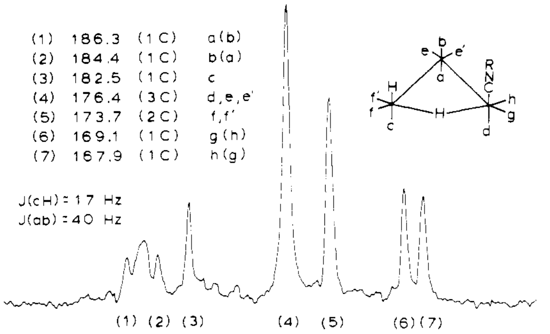

Figure 4. ^{13}C NMR spectrum of ca. 50% ^{13}CO-enriched $H_2Os_3(CO)_{10}(CNMe)$ at −70 °C in acetone-d_6.

of ^1H NMR resonances, each set similar to those of the other adducts. However, the $^{13}C\{^1H\}$ NMR spectrum of $H_2Os_3(CO)_{10}(CNMe)$ in the slow-exchange limit exhibits only one set of carbonyl resonances (Figure 4). At −70 °C the spectrum consists of seven signals (in acetone-d_6): (1) 186.3 (1 C), (2) 184.4 (1 C), (3) 182.5 (1 C), (4) 176.4 (3 C), (5) 173.7 (2 C), (6) 169.1 (1 C), and (7) 167.9 (1 C) ppm. Resonance 3 is assigned to the axial carbonyl trans to the axial, terminal hydride on the basis of the similarity of the chemical shift to that of the analogous carbonyl of $H_2Os_3(CO)_{10}(PMe_2Ph)$ and its strong coupling of 17 Hz to the hydride. Resonances 1 and 2 are assigned to the axial carbonyls on the unsubstituted $Os(CO)_4$ fragment because of the ^{13}C–^{13}C coupling of ca. 40 Hz between them (estimated ^{13}C enrichment of 40%); the axial ^{13}C–axial ^{13}C coupling constant is between 30 and 40 Hz for other triosmium clusters, including $Os_3(CO)_{10}(C_7H_8)$ (35 Hz).[19] The remaining seven carbonyls have very similar ^{13}C chemical shifts. The spectrum is consistent with the solid-state structure found for $H_2Os_3(CO)_{10}(CN\text{-}t\text{-}Bu)$ with an axially coordinated isocyanide ligand. Then the large difference in the chemical shifts of resonances 1 and 2 is readily explained by the effect of the axial isocyanide on the chemical shift of the adjacent axial carbonyl. Resonances 6 and 7 are assigned to the equatorial carbonyls on the $Os(CO)_3(CNMe)$ fragment. While phosphine substitution results in downfield shifts for the remaining carbonyls, substitution by isocyanides seems to cause upfield shifts for the other carbonyls, relative to carbonyls on unsubstituted osmium atoms.[16] Resonance 4 is assigned to isochronous equatorial carbonyls on the $Os(CO)_4$ fragment, which are relatively unshifted, and the axial carbonyl trans to the methyl isocyanide ligand, which is shifted upfield by the effects of the bridging hydride and the trans isocyanide ligand. Resonance 5 is assigned to accidentally isochronous equatorial carbonyls cis to the terminal hydride. Due to the axial isocyanide ligand, the two isomers observed in the ^1H NMR spectrum must differ in the orientation of the axial hydride relative to the side of the triosmium plane occupied by the isocyanide ligand. However, the chemical shifts of the analogous carbonyl ligands of the two isomers must be coincidentally identical.

The dynamic ^{13}C NMR behavior of $H_2Os_3(CO)_{10}(CNMe)$ is qualitatively similar in the intermediate-exchange region to that for $H_2Os_3(CO)_{10}L$, L = $P(C_6H_5)_3$ or $P(CH_3)_2(C_6H_5)$. At −13 °C the resonance at 182.5 ppm, assigned to the axial carbonyl trans to the terminal hydride, and one of the overlapping carbonyl signals at 173.7 ppm, assigned to one of the equatorial carbonyls cis to the terminal hydride, have disappeared into the base line. No other changes are observed. However, the limiting fast-exchange spectrum could not be obtained due to the rearrangement to $HOs_3(\mu\text{-}CNHCH_3)(CO)_{10}$ at room temperature.[4,5]

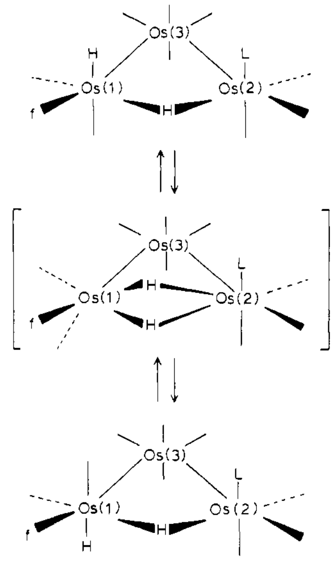

Figure 5. Fluxional process proposed for $H_2Os_3(CO)_{10}L$, where L occupies an axial position.

The ^{13}C NMR spectrum of $H_2Os_3(CO)_{10}(CN\text{-}t\text{-}Bu)$ at −45 °C in deuteriodichloromethane is very similar to that of $H_2Os_3(CO)_{10}(CNCH_3)$ but is better resolved. The spectrum consists of nine lines: (1) 185.4 (1 C), (2) 184.3 (1 C), (3) 181.5 (1 C), (4) 175.9 (1 C), (5) 175.6 (2 C), (6) 173.7 (1 C), (7) 173.1 (1 C), (8) 168.6 (1 C), and (9) 168.0 (1 C) ppm. No evidence for the presence of two isomers could be obtained from this spectrum. The large coupling (J = 39 Hz) between resonances 1 and 2 allows their assignment to the trans axial carbonyls on the $Os(CO)_4$ fragment. The ^{13}C–^1H coupling of 21 Hz for resonance 3 to the terminal hydride marks it as the axial carbonyl trans to the terminal hydride. Resonances 7 and 9 have unresolved coupling to both the terminal and bridging hydrides and, thus, must be due to the equatorial carbonyls cis to the terminal hydride. At 25 °C resonances 3 and 7 have collapse into the base line. Again decomposition prevents observation of coalescence.

If the same type of fluxional process is occurring for the isocyanide adducts as is occurring for the phosphine adducts, the rearrangement will *not* make the two sides of the triosmium plane equivalent (Figure 5). Thus, the limiting fast-exchange spectra should retain the ^{13}C–^{13}C coupling between the axial carbonyls of the $Os(CO)_4$ unit. While these spectra cannot be obtained, the coalescence temperature for resonances 1 and 2 of $H_2Os_3(CO)_{10}(CNMe)$ should be ca. −6 °C, while that for resonances 3 and 5 is calculated to be ca. +11 °C. Since at −13 °C the axial–axial ^{13}C coupling is still observed, even though resonances 3 and 5 are significantly broadened, these axial carbonyls are not being rendered equivalent by the fluxional process.

The proposed mechanism predicts further that with axially substituting ligands the two isomers are interconverted with each exchange (Figure 5). In this process the axial and bridging hydrides within each isomer are not interconverted. Rather, the axial hydride of one isomer exchanges with the bridging hydride of the second isomer, and vice versa. The free energies of activation for the fluxional process, as measured by line broadening for each isomer separately, should differ by the standard free energy difference between the isomers. In fact, it is calculated from line broadening for each isomer of $H_2Os_3(CO)_{10}(CN\text{-}t\text{-}Bu)$ that $\Delta G^{\ddagger}$ for exchange out of the major isomer is 13.2 kcal/mol, while $\Delta G^{\ddagger}$ for exchange out of the minor isomer is 12.8 kcal/mol. From the equilibrium constant measured from ^1H NMR integrals at the same temperature, ΔG° for the major isomer to minor isomer conversion is 0.4 kcal/mol. Computer simulations (Figure 6)

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[19] M. Tachikawa, S. I. Richter, and J. R. Shapley, *J. Organomet. Chem.*, **128**, C9 (1977).

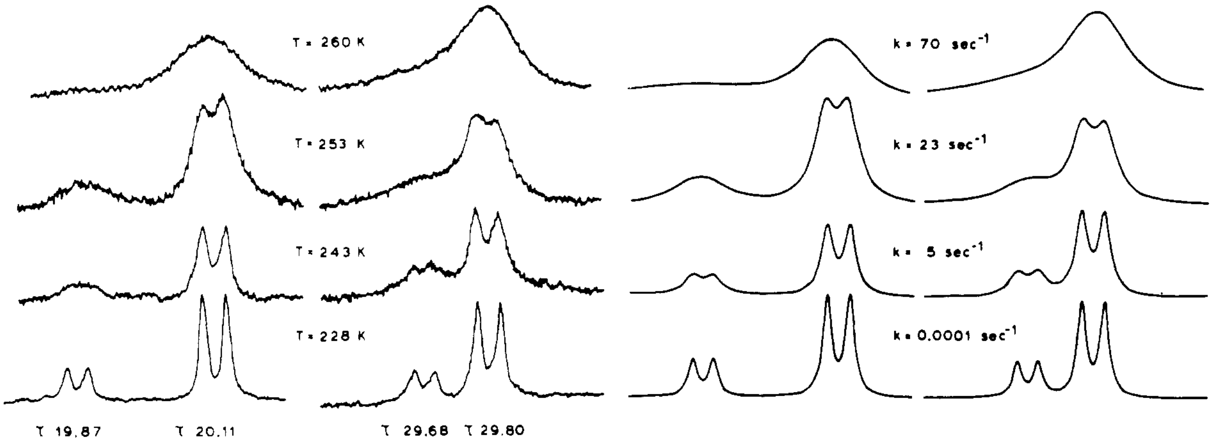

Figure 6. Experimental and computer-simulated ^1H NMR spectra for $H_2Os_3(CO)_{10}(CN\text{-}t\text{-}Bu)$.

of exchange of the low-field hydride resonance of one isomer with the high-field resonance of the other isomer compare well with the experimental spectra.

Additional evidence for the nature of the fluxional process was obtained via a spin saturation labeling experiment.[20] The ^1H NMR spectrum of $H_2Os_3(CO)_{10}(CN\text{-}t\text{-}Bu)$ at ca. −40 °C was recorded. Then, while the high-field hydride signals of the two isomers were observed, selective irradiation of each of the low-field hydride signals was performed. When the low-field signal of the minor isomer was saturated, the high-field resonance of the minor isomer sharpened to a singlet and the intensity of the high-field resonance of the major isomer was substantially reduced. Thus, the exchange of the low-field hydride of the minor isomer transfers a nonequilibrium nuclear spin distributon to the high-field hydride of the major isomer. Alternatively spin saturation of the low-field signal of the major isomer leads to reduced intensity of the high-field signal of the minor isomer.

Variation of $\Delta G^\ddagger$ with L. The free energy of activation for hydride interchange in $H_2Os_3(CO)_{10}L$ determined from ^1H NMR line broadening near the slow-exchange limit varies between 11.2 and 13.5 kcal/mol, depending on the steric and electronic character of L. A complete list of our results is given in Table I. While it was not possible to obtain entropies and enthalpies of activation because of the small temperature range over which the spectra could be observed, comparison of free energies of activation for the various adducts should be meaningful for closely related complexes. Too few adducts with axially coordinated ligands have been studied to make generalizations about the variation of $\Delta G^\ddagger$ for these complexes with L, and in addition, the values measured for these adducts are the same within experimental error. Therefore, the adducts of CNMe, CN-*t*-Bu, $4\text{-}NC_5H_4Me$, and $4\text{-}NC_5H_4Br$ will not be considered further.

Two trends can be discerned. First, the free energy of activation increases as the steric demand of the ligand increases. This trend is illustrated best by the series PMe_3 (11.3 kcal), PEt_3 (12.0 kcal), and $P(C_6H_{11})_3$ (13.5 kcal), for which the cone angles are 118, 132, and 170°, respectively.[21] Also compare the values for $P(OMe)_3$ (12.3 kcal) and $P(O\text{-}i\text{-}Pr)_3$ (12.8 kcal) with their cone angles of 108 and 131°. However, electronic effects are also important. For ligands of similar size within a homologous series, lower free energies of activation are associated with more basic ligands. For example, PEt_3, a very strong electron-donor ligand, produces a much lower value for $\Delta G^\ddagger$ (12.0 kcal/mol) than $P(OPh)_3$ (13.1 kcal/mol) even though both have cone angles of ca. 130°. However, for ligands containing donor atoms from different rows of the Periodic Table increasing basicity does *not* correlate with decreasing free energy of activation; the order of increasing basicity is in fact the order of *increasing* $\Delta G^\ddagger$: $SbPh_3 < AsPh_3 < PPh_3$ and $AsMe_2Ph < PMe_2Ph$. These results can be more readily related to the polarizability of the donor atom, which is related to basicity only for homologous series. Consistent with this, the order of increasing free energy of activation for adducts with halide ions is $L = I^-$ (11.5 kcal) $< Br^-$ (11.9 kcal) $< Cl^-$ (12.2 kcal)—the order of increasing basicity but decreasing polarizability. In general, it appears that the value for the free energy of activation for hydride exchange in $H_2Os_3(CO)_{10}L$ decreases as the polarizability of the donor atom of L increases and increases as the size of L increases. Similar steric and electronic effects have been noted for protonation of iridium complexes.[22]

The transition state for hydride and carbonyl exchange must have equivalent hydride ligands, either both bridging or both terminal. The variation of $\Delta G^\ddagger$ with the steric and electronic properties of L strongly suggests a doubly bridging configuration (Figure 3). In this case Os(2) is six-coordinate in the ground state but seven-coordinate in the transition state; bulky ligands thus increase the free energy of activation for hydride excchange. A transition state with two terminal hydrides on Os(1) would make Os(2) six-coordinate, just as in the ground state, and bulky ligands might be expected either to decrease the free energy of activation or to have no effect.

The effect of the electronic properties of L upon the free energy of activation for hydride exchange in $H_2Os_3(CO)_{10}L$ can also be accommodated by the proposed transition state. The bonding of bridging hydride ligands is a three-center, two-electron interaction, and hydrides seem to prefer to bridge to centers of higher electron density.[23] Presumably, this is why the bridging hydride spans the edge to the phosphine-substituted metal atom of $H_2Os_3(CO)_{10}(PPh_3)$, rather than to the unsubstituted metal atom. Since the transition state has one more bridging hydride than the ground state, the Os atom to which the bridge is formed should have a lower electron density in the transition state than in the ground state. Polarizable ligands may reduce the difference in charge distribution between the ground and transition states and, thus, lower the activation energy for exchange.

The fluxional process for $H_2Os_3(CO)_{10}L$ is very similar to that observed for $H_4Re_4(CO)_{15}^{2-}$, the only other cluster re-

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(21) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).

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(23) For example, protonation of $Os_3(CO)_{11}(PMePh_2)$ occurs at the metal–metal bond adjacent to the site of substitution (A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 2967 (1970)), and substitution of $(\mu\text{-}H)(\mu\text{-}S_2CH)Os_3(CO)_{10}$ to give $(\mu\text{-}H)(\mu\text{-}S_2CH)Os_3(CO)_9(PMe_2Ph)$ causes migration of the bridging hydride to a position adjacent to the site of substitution (R. D. Adams and J. P. Selegue, *J. Organomet. Chem.*, **195**, 223 (1980)).

ported to have both terminal and bridging hydrides.[24] It is likely that the turnstile mechanism established for bridge–terminal exchange in $H_2Os_3(CO)_{10}L$ is a general mechanism in cluster compounds of this type.

Experimental Section

Starting Materials. $Os_3(CO)_{12}$ was prepared by the method of Nyholm et al.[25] from osmium tetraoxide (Engelhard). The synthesis of $H_2Os_3(CO)_{10}$ is described by Kaesz et al.,[12] and $D_2Os_3(CO)_{10}$ was prepared in the same way with use of deuterium gas but by recrystallizing from carbon tetrachloride instead of purifying by chromatography. Organic compounds synthesized for this study by using literature procedures were dimethylphenylphosphine,[26] trimethylphosphine,[27] methyl isocyanide,[28] and *tert*-butyl isocyanide.[29] Other ligands were obtained from commercial sources.

Physical Methods for Characterization. Infrared spectra were obtained on Beckman IR-10 and Perkin-Elmer 467 spectrophotometers, usually as cyclohexane solutions. Calibration was accomplished by using the 2138.5-cm^{-1} absorption of cyclohexane or by using polystyrene. Proton NMR spectra were recorded on a Varian HA-100 spectrometer with a Varian Model 6040 variable-temperature controller. Some spectra were obtained with JEOLCO FX-60 or Varian A60-A instruments. The ^{13}C NMR spectra were obtained with JEOLCO FX-60 (15.03 MHz) or Varian XL-100 (25.2 MHz) spectrometers with ca. 0.02 M $Cr(acac)_3$ added to the samples as relaxation agent. Samples enriched with ^{13}CO were prepared from ca. 60% enriched $Os_3(CO)_{12}$. Mass spectra were obtained by the staff of the School of Chemical Sciences Mass Spectroscopy Laboratory either with a Varian MAT CH-5 instrument (electron impact, 70 eV) or with a Varian 731 instrument (field desorption). Elemental analyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences. Melting points were taken on a Buchi melting point apparatus in capillaries sealed under vacuum.

$H_2Os_3(CO)_{10}(P(c\text{-}C_6H_{11})_3)$. Tricyclohexylphosphine was added as a deuteriochloroform solution to a solution of $H_2Os_3(CO)_{10}$ (34 mg) in the same solvent, and the solution was used to obtain NMR spectra. After 4 days at −25 °C, the solution was applied to a silica gel preparative TLC plate and eluted with 25% benzene in petroleum ether. Only one major band was observed, although three minor impurities were present. After extraction with dichloromethane, the residue of the major product was recrystallized from methanol to give $H_2Os_3(CO)_{10}(P(c\text{-}C_6H_{11})_3)$ (31 mg, 65%). Mp: 140–144 °C dec. MS (^{192}Os): m/z 1139 ± 1 (field desorption). Anal. Calcd for $Os_3C_{28}H_{35}O_{10}P$: C, 29.66; H, 3.12; Os, 50.36. Found: C, 29.41; H, 3.13; Os, 50.52. IR (C_6H_{12}): ν_{CO} 2102 (m), 2059 (s), 2048 (s), 2020 (vs), 2012 (vs), 2000 (s), 1994 (s), 1981 (m, sh), 1978 (m), 1968 (m) cm^{-1}.

$H_2Os_3(CO)_{10}(PMePh_2)$. To a solution of $H_2Os_3(CO)_{10}$ (40 mg) in deuteriochloroform was added enough methyldiphenylphosphine to discharge the purple color due to $H_2Os_3(CO)_{10}$. The solvent was stripped off, and the residue was recrystallized from methanol to give yellow crystalline $H_2Os_3(CO)_{10}(PMePh_2)$ (21 mg, 42%). Mp: 117–122 °C dec. MS (^{192}Os): m/z 1059 ± 1 (field desorption). Anal. Calcd for $Os_3C_{23}H_{15}O_{10}P$: C, 26.23; Os, 54.20. Found: C, 27.02; Os, >49.1. IR (C_6H_{12}): ν_{CO} 2105 (m), 2065 (s), 2050 (s), 2023 (vs), 2018 (s, sh), 2010 (m, sh), 2000 (sh), 1990 (m), 1984 (m), 1973 (m) cm^{-1}.

$H_2Os_3(CO)_{10}(AsPh_3)$. To a solution of $H_2Os_3(CO)_{10}$ (35 mg) in dichloromethane was added enough triphenylarsine to discharge the purple color. After evaporation of solvent, the residue was recrystallized from methanol to give $H_2Os_3(CO)_{10}(AsPh_3)$ (17 mg, 36%) as yellow crystals. MS (^{192}Os): m/z 1136 (electron impact). Anal. Calcd for $Os_3C_{28}H_{17}O_{10}As$: C, 29.00; Os, 49.25. Found: C, 29.40; Os, 49.37. IR (C_6H_{12}): ν_{CO} 2106 (m), 2067 (s), 2052 (s), 2024 (vs), 2018 (s), 2008 (m), 2000 (m), 1984 (m), 1974 (m) cm^{-1}.

$H_2Os_3(CO)_{10}(AsMe_2Ph)$. This compound was prepared in 64% yield by the method described for $H_2Os_3(CO)_{10}(AsPh_3)$. MS (^{192}Os): m/z 1040 (electron impact). Anal. Calcd for $Os_3C_{18}H_{13}O_{10}As$: C, 20.88; H, 1.27; Os, 55.15. Found: C, 20.88; H, 1.30; Os, 54.77. IR (C_6H_{12}): ν_{CO} 2109 (w), 2068 (s), 2054 (s), 2026 (vs), 2019 (vs), 2008 (m), 1997 (w), 1984 (vw), 1973 (vs) cm^{-1}.

$H_2Os_3(CO)_{10}(P(OMe)_3)$. Trimethyl phosphite was added dropwise to a stirred solution of $H_2Os_3(CO)_{10}$ (42 mg) in 6 mL of pentane until the purple color was discharged. The solution was cooled to −25 °C. After 2 days bright yellow crystals of $H_2Os_3(CO)_{10}(P(OMe)_3)$ were collected and washed first with pentane and then with methanol: yield 29 mg, 60%. Anal. Calcd for $Os_3C_{13}H_{11}O_{13}P$: C, 15.97; H, 1.14; Os, 58.42. Found: C, 16.24; H, 1.07; Os, 58.07. IR (C_6H_{12}): ν_{CO} 2112 (w), 2071 (s), 2053 (s), 2030 (vs), 2021 (m), 2013 (m), 2006 (m), 1992 (w), 1986 (m), 1974 (m) cm^{-1}.

Determination of Rates of Hydride Interchange for $H_2Os_3(CO)_{10}L$. Rates of hydride interchange in these complexes were measured from the line broadening of the hydride NMR signals near the slow-exchange limit. Samples were generally prepared by adding 1 equiv or a slight excess of ligand to a dichloromethane solution of $H_2Os_3(CO)_{10}$. Adducts with anionic Lewis bases were obtained by dissolving $H_2Os_3(CO)_{10}$ in a saturated acetone-d_6 solution of the appropriate salt (KI, KBr, LiCl, NaN_3, KSCN, or KCN). The spectra in some cases were obtained in deuteriochloroform, acetone-d_6, or chlorobenzene. When the same complex was examined in two different solvents, no significant difference in the rates was observed. Where appropriate, the free and coordinated ligand resonances were monitored to check for ligand exchange at the temperatures used for the kinetic data. No evidence for exchange of free and coordinated ligands on the NMR time scale was obtained. In most cases spectra were recorded on a Varian HA-100 spectrometer with a Model 6040 temperature controller. The spectra were generally accumulated at 50-Hz expansion on a Varian 1024 CAT computer because of low signal intensity due to limited solubility and/or extensive broadening. Where phosphorus coupling to the upfield hydride prevented accurate measurements, only the downfield hydride signal was used for data. Spectra (usually three) were obtained at as many temperatures (ca. 5 °C intervals) as possible between the temperature at which broadening was first noted and the temperature at which the signals were too broad to be observed. For $H_2Os_3(CO)_{10}(PMe_2Ph)$ the line narrowing of the coalesced signal was also used to approximate the rate constant and the free energy of activation for exchange near the fast-exchange limit. However, the values obtained are not reliable due to the poor quality of the spectra and the inability to measure the limiting fast-exchange line width. In all cases, decomposition occurred before the limiting fast-exchange spectrum could be obtained.

Rate constants at each temperature were determined by comparison of the line widths of the experimental spectra with those of spectra calculated by using a program adapted by S. I. Richter from that developed by Binsch.[30] Temperature measurements were made from methanol chemical shifts according to the method of van Geet.[31] Once rate constants were determined, the value of the free energy of activation at each temperature was calculated by using the equation ΔG^{*} (cal/mol) = $4.57T(10.318 - \log (k/T))$, where k is in s^{-1}, and T is in K. The average of the ΔG^{*} values for each complex was taken and the estimated error taken as the standard deviation. Reproducibility of ΔG^{*} is ±0.2 kcal/mol or better. Errors in the temperature measurement, estimated by van Geet to be ±1 K, and the range in values of k that could match a given spectrum contribute to the uncertainty in ΔG^{*}.

Spin-Saturation Labeling of the Hydrides of $H_2Os_3(CO)_{10}(CN\text{-}t\text{-}Bu)$. The sample was prepared by the dropwise addition of *tert*-butyl isocyanide to a dichloromethane solution of $H_2Os_3(CO)_{10}$ (39 mg). The spectra were recorded on a Varian HA-100 instrument equipped with a Varian Model 6040 variable-temperature controller and two external oscillators. The probe was cooled to ca. −40 °C to increase the lifetime of the minor isomer to ca. 0.2 s. Spectra of all four hydride

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(27) W. Wolfsberger and H. Schmidbauer, *Synth. React. Inorg. Met.-Org. Chem.*, **4**, 149 (1974).

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(29) I. Ugi, R. Meyr, M. Lipinski, F. Bodesheim, and F. Rosendahl, "Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 300.

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(31) (a) A. L. van Geet, *Anal. Chem.*, **42**, 679 (1970); (b) *ibid.*, **40**, 2227 (1968).

resonances were recorded, and then, with the observing oscillator set at 2530 Hz upfield from the dichloromethane lock to record the upfield hydrides, selective saturation of each of the lower field hydrides was performed. Upon irradiation at 1522 Hz upfield from lock (the minor isomer), the high-field resonance for the minor isomer sharpened to a singlet and the resonance for the major isomer collapsed to a weak doublet. The integrated intensities, determined by cutting and weighing, gave relative intensities of 0.63 for the minor isomer and 0.37 for the major isomer hydride signals. Upon irradiation at 1544 Hz upfield from lock (the major isomer), the upfield resonance of the major isomer became a singlet and the resonance for the minor isomer collapsed to a weak doublet, with relative intensities 0.94 and 0.06, respectively. In the absence of spin saturation, the relative intensities were 0.27 for the minor isomer and 0.73 for the major isomer.

Acknowledgment. This work was supported by a grant from the National Science Foundation. J.B.K. gratefully acknowledges a NSF Predoctoral Fellowship (1975–1977).

Registry No. $H_2Os_3(CO)_{10}$, 41766-80-7; $H_2Os_3(CO)_{10}(P(c\text{-}C_6H_{11})_3)$, 82456-47-1; $H_2Os_3(CO)_{10}(PMePh_2)$, 82456-48-2; $H_2Os_3(CO)_{10}(AsPh_3)$, 82456-49-3; $H_2Os_3(CO)_{10}(AsMe_2Ph)$, 56398-28-8; $H_2Os_3(CO)_{10}(P(OMe)_3)$, 82456-50-6; $H_2Os_3(CO)_{10}(CN\text{-}t\text{-}Bu)$, 69942-19-4; $H_2Os_3(CO)_{11}$, 56398-24-4; $H_2Os_3(CO)_{10}(PPh_3)$, 56398-26-6; $H_2Os_3(CO)_{10}(PMe_2Ph)$, 56398-27-7; $H_2Os_3(CO)_{10}(PMe_3)$, 82456-51-7; $H_2Os_3(CO)_{10}(PEt_3)$, 82456-52-8; $H_2Os_3(CO)_{10}(PBu_3)$, 82456-53-9; $H_2Os_3(CO)_{10}(P(OEt)_3)$, 82456-54-0; $H_2Os_3(CO)_{10}(P(O\text{-}i\text{-}Pr)_3)$, 77759-82-1; $H_2Os_3(CO)_{10}(P(OPh)_3)$, 82456-55-1; $H_2Os_3(CO)_{10}(P(OCH_2)_3CC_2H_5)$, 82456-56-2; $H_2Os_3(CO)_{10}(SbPh_3)$, 82456-57-3; $H_2Os_3(CO)_{10}(CNMe)$, 70810-41-2; $H_2Os_3(CO)_{10}(4\text{-}NC_5H_4Me)$, 82456-58-4; $H_2Os_3(CO)_{10}(4\text{-}NC_5H_4Br)$, 82456-59-5; $H_2Os_3(CO)_{10}I^-(K^+)$, 82456-60-8; $H_2Os_3(CO)_{10}Br^-(K^+)$, 82456-61-9; $H_2Os_3(CO)_{10}Cl^-(Li^+)$, 82456-62-0; osmium, 7440-04-2.

Supplementary Material Available: Infrared spectral data (Table A) and ^1H NMR spectral data (Table B) for $H_2Os(CO)_{10}L$ and infrared spectra of $H_2Os_3(CO)_{11}$ and $D_2Os_3(CO)_{11}$ (Figure X) (6 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Chimica Analitica and Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy,
the Instituto de Quimica, Universidade Federal da Bahia, Salvador Bahia, Brazil,
and the Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR,
Univesità di Parma, 43100 Parma, Italy

Chemistry and Structure of an Inorganic Analogue of a Carboxylic Acid: Hydroxobis(8-quinolinato)oxovanadium(V)

AMBROGIO GIACOMELLI,[1a] CARLO FLORIANI,*[1b] ADALCINDO OFIR DE SOUZA DUARTE,[1c]
ANGIOLA CHIESI-VILLA,[1d] and CARLO GUASTINI[1d]

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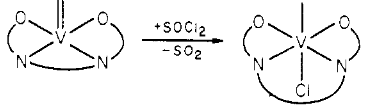
Basic hydrolysis, under mild conditions, of (μ-oxo)bis[bis(8-quinolinato)oxovanadium(V)], $[(Q_2VO)_2O]$ (Q = 8-quinolinato anion), obtained by a one-step synthesis, gave a dioxovanadium(V) complex, $[Q_2VO_2]^-$, containing the VO_2^- unit. The structure of this anionic species was determined by an X-ray analysis carried out on the corresponding salts $\{[Q_2VO_2Na(H_2O)_2]_2(\mu\text{-DMF})\}$ (VI) and $\{[Q_2VO_2](n\text{-}Bu_4N)\cdot H_2O\}$ (VII). The VQ_2 unit has similar structural characteristics in both complexes, with the two N donor atoms trans to the oxo groups, which have a cis configuration. The V–N bonds, as a consequence, have the longest distances so far encountered ($V\text{–}N_{av}$ = 2.33 Å). Complex VI is a dimer, where two VO_2 units are bridged by two Na^+ ions sharing the oxygen of a DMF molecule. In complex VII the oxygen is only weakly bonded to a H_2O molecule, via hydrogen bonding. In both complexes the structural data concerning the VO_2 units are very close, with a V–O–V angle varying from 105.7 (2)° in complex VI to 106.1 (5)° in complex VII, while the V–O bond distances have a double-bond character [1.647 (4) and 1.628 (2) Å in complex VI; 1.62 (1) Å in complex VII]. The O···O bite values are 2.610 (4) Å (complex VI) and 2.58 (1) Å (complex VII). These results invite comparison of the VO_2^- unit with the carboxylato group RCO_2^-. The relationship between other vanadium(V) derivatives and organic functional groups related to a carboxylic acid is reported. The inorganic analogue of a carboxylic acid itself is obtained on acidifying an aqueous solution of $[Q_2VO_2]^-$. $[Q_2V(O)(OH)]$, which is a very well-known analytical reagent for organic compounds, was found to be a weak acid with a pK_A of 6.3. Crystallographic details for $\{[Q_2VO_2Na(H_2O)_2]_2(\mu\text{-DMF})\}$: space group *Pbcn* (orthorhombic); a = 30.245 (2), b = 9.744 (1), c = 14.167 (1) Å; V = 4175.1 Å^3; Z = 4. The final R factor was 4.7% for 2867 observed data. Crystallographic details for $\{[Q_2VO_2](n\text{-}Bu_4N)\cdot H_2O]\}$: space group $I\bar{4}2d$ (tetragonal); a = b = 19.04 (3), c = 19.486 (3) Å; V = 7064.1 Å^3; Z = 8. The final R factor was 5.9% for 568 observed data.

Introduction

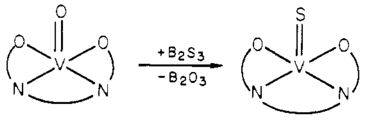
In recent years, a very useful correlation between inorganic and organic chemistry has been proposed in pointing out the analogies between d^8 square-planar complexes and carbenes, or d^7 or d^9 metal complexes and free radicals.[2]

In the present work we develop the chemistry of the metal–X fragment (X = oxygen, sulfur, or nitrogen) and show this to have structural and chemical features in common with the corresponding organic functional groups C–X. Such relationships are useful in suggesting the following points.

(i) Reaction of the Metal–X Units by Using Reactions Similar to Those Applied to the Corresponding C–X Functional Groups in Organic Chemistry. It was reported that the "V═O" ketonic-like unit, supposed to be unreactive, can be transformed as follows:[3]



(ref 3a)



(ref 3b)

ONNO ≡ salen ≡ *N,N'*-ethylenebis(salicylideneaminato) dianion

The synthesis of a metal–nitrene unit (M═NR), the inorganic

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(1) (a) Istituto di Chimica Analitica, Università di Pisa. (b) Istituto di Chimica Generale, Università di Pisa. (c) Universidade Federal da Bahia. (d) Università di Parma.

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