the above restraint. The energy maximum in this curve occurs at $R = 2.7$ Å. At this value for R, the H–C–Fe angle is 108°, the C(H)–Fe–C angles are about 99°, and incoming C–Fe–C angles are about 87°. The saddle point occurs at the relatively long Fe–C distance of 2.7 Å for this case of attack on the tetrahedral complex, whereas in the case of attack on the trigonal-bipyramid complex, the energy maximum occurs at $R = 2.1$ Å where the CO is almost in to its equilibrium position. In this latter case the activated complex is very product like. For the energy curve with attack on the tetrahedral unstable intermediate, the energy zero is taken as the separated CO and the trigonal-bypyramid hydride complex. Thus, right to begin with, this curve incorporates the energy rise of the hydride migration.

The major factor in the activation energy is the migration of the H atom in all cases. For attack on a tetrahedral complex this has already occurred so the saddle point occurs early in the CO attack, while for a concerted mechanism, the attack on a trigonal-bipyrimid hydride has the saddle point occurring after the CO has almost reached its equilibrium position with respect to the Fe atom when the H atom has almost completed its migration.

Cis CO Addition to Tetrahedral ((CO)$_3$FeCHO)$^-$. Calculations have been done for structure VI as the CO group approaches in the xz plane cis to the formyl group. The energy as a function of R, the incoming C distance to the Fe atom is shown in Figure 3. This calculation was done in the same manner as for the trans attack with the incoming CO having the additional freedom to vary the C(H)–Fe–C angle. Again the energy maximum occurs at the relatively long Fe–C distance of 2.5 Å. At the activated complex the H–C–Fe angle is 106° while the CO groups have moved from 1 to 13° toward the trigonal-bipyramid angles. The incoming C–Fe–C(H) angle is 85°. Thus the cis attack is remarkably like the trans attack.

The three activation energies are close enough that none can be eliminated on the basis of this calculational model. In all cases the major factor in the activation energy is the hydride migration.

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Registry No. I, 18716-80-8; II, 96760-12-2; III, 48055-09-0; Fe(CO)$_5$, 13463-40-6; ((CO)$_3$FeCHO)$^+$, 96760-13-3; FeH, 15600-68-7; CH$_3$CHO, 75-07-0.

Mechanisms of the Elimination Reactions of Os(CO)$_4$(H)R and Os(CO)$_4$R$_2$

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Kinetic and labeling studies of alkane elimination from *cis*-Os(CO)$_4$(H)R have shown that the rate-determining step is isomerization of *cis*-Os(CO)$_4$(H)R to a reactive intermediate (probably an acyl hydride); this intermediate can then react either with unisomerized *cis*-Os(CO)$_4$(H)R to give intermolecular R–H elimination (and HOs(CO)$_4$Os(CO)$_4$R) or with another nucleophile L to give intramolecular R–H elimination (and Os(CO)$_4$L). The *cis*-Os(CO)$_4$(H)R is slightly more reactive toward the intermediate than are phosphines and phosphites, including Et$_3$P. The formation of methane from *cis*-Os(CO)$_4$(CH$_3$)$_2$ proceeds via an intermediate (most likely a methyl radical) which displays high H/D selectivity in attacking alkane solvents. The formation of ethylene and ethane from *cis*-Os(CO)$_4$(C$_2$H$_5$)$_2$ involves a reversible β-hydrogen elimination; thus the ethylene from *cis*-Os(CO)$_4$(C$_2$H$_5$)$_2$ and *cis*-Os(CO)$_4$(C$_2$D$_5$)$_2$ contains all possible H/D isomers. Simple intramolecular reductive elimination has not been observed from any *cis*-Os(CO)$_4$RR′.

As evidence has accumulated[1] that dinuclear elimination is involved in cobalt-catalyzed hydroformylation, the intermolecular formation of C–H bonds from organometallic precursors has received increasing attention. Systems investigated include *cis*-Os(CO)$_4$(H)R,[2] CpMo(CO)$_3$R/CpMo(CO)$_3$H,[3] various alkyl complexes/CpV(CO)$_3$H$^-$,[3b] and *cis*-Mn(CO)$_4$LR/*cis*-Mn(CO)$_4$LH (L = CO or tertiary phosphine).[4]

The Os(CO)$_4$(H)R system originally attracted our attention because these hydrido alkyls were less stable than either *cis*-Os(CO)$_4$H$_2$ or the corresponding dialkyls. The hydrido methyl and hydrido ethyl complexes nevertheless proved sufficiently stable to permit their preparation[5] and manipulation on a vacuum line at room temperature. We now present a complete account of our kinetic and mech-

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anistic results on the thermolysis of $Os(CO)_4(H)R$ (R = Me, Et) and, for comparison, some results on other binuclear eliminations and on the thermolysis of $Os(CO)_4R_2$.[6]

Results

The Elimination of Alkanes from *cis*-$Os(CO)_4(H)R$. The formation of a binuclear product (reaction 1) in the thermal decomposition of *cis*-$Os(CO)_4(H)R$[5] did not by itself mean that the elimination was intermolecular.

$$2cis\text{-}Os(CO)_4(H)R \xrightarrow{\Delta} (OC)_4HOs\text{–}OsR(CO)_4 + R\text{–}H \quad (1)$$

$$R = Me, 49\ °C;\ R = Et, 28\ °C$$

$Os(CO)_4$, formed by *intramolecular* alkane elimination from $Os(CO)_4(H)R$ (reaction 2), could have formed the binuclear product by insertion into the Os–H bond of another molecule of $Os(CO)_4(H)R$ (reaction 3).

$$cis\text{-}Os(CO)_4(H)R \rightarrow Os(CO)_4 + R\text{–}H \quad (2)$$

$$Os(CO)_4 + cis\text{-}Os(CO)_4(H)R \rightarrow (OC)_4HOs\text{–}OsR(CO)_4 \quad (3)$$

Determination of the inter- or intramolecular nature of the methane-forming process required appropriately-labeled derivatives of $Os(CO)_4(H)R$. These proved available by appropriate modifications (reactions 4–7) of our syntheses[5] of the unlabeled compounds. $C_2D_5OSO_2F$ was prepared from ethanol-d_6 via $(C_2D_5)_2SO_4$ by the method described by Whiting et al.[7] for the preparation of the undeuterated compound.

$$[Os(CO)_4H]^- + CD_3OSO_2F \xrightarrow[\text{tetraglyme}]{25\ °C} cis\text{-}Os(CO)_4(H)CD_3 \quad (4)$$

$$[Os(CO)_4]^{2-} \xrightarrow{CF_3CO_2D} [Os(CO)_4D]^- \xrightarrow[\text{tetraglyme}]{CH_3OSO_2F} cis\text{-}Os(CO)_4(D)CH_3 \quad (5)$$

$$[Os(CO)_4H]^- + C_2D_5OSO_2F \xrightarrow[\text{tetraglyme}]{25\ °C} cis\text{-}Os(CO)_4(H)C_2D_5 \quad (6)$$

$$[Os(CO)_4]^{2-} \xrightarrow{CF_3CO_2D} [Os(CO)_4D]^- \xrightarrow[\text{tetraglyme}]{EtOSO_2F} cis\text{-}Os(CO)_4(D)C_2H_5 \quad (7)$$

Crossover experiments showed the formation of mixed-alkane products (eq 8 and 9). The CD_3H/CD_4 ratio from

$$Os(CO)_4(H)CD_3 + Os(CO)_4(D)CH_3 \xrightarrow[\text{methylcyclohexane}]{49\ °C} CD_4 + CD_3H + CH_3D + CH_4 \quad (8)$$

$$Os(CO)_4(H)C_2D_5 + Os(CO)_4(D)C_2H_5 \xrightarrow[n\text{-octane}]{35\ °C} C_2D_6 + C_2D_5H + \text{other deuterated ethanes} \quad (9)$$

the thermolysis of a mixture of $Os(CO)_4(H)CD_3$ and $Os(CO)_4(D)CH_3$ [assumed to reflect the relative reactivity of the hydride in $Os(CO)_4(H)CD_3$, and the deuteride in $Os(CO)_4(D)CH_3$, toward the CD_3 group in $Os(CO)_4(H)CD_3$] indicated a small primary kinetic isotope effect (k_H/k_D about 1.1); a similar assumption gave the same small primary isotope effect (1.1) from the C_2D_5H/C_2D_6 ratio from the thermolysis of an $Os(CO)_4(H)C_2D_5/Os(CO)_4(D)C_2H_5$ mixture.

Table I. First-Order Rate Constants for the Disappearance of *cis*-$Os(CO)_4(H)R$ by Alkane Elimination According to Reaction 1 (No Added Nucleophile)

R	solvent	T, °C	10^5k_1,[a] s^{-1}	$[Os(CO)_4(H)R]_0$, M
Me	methylcyclohexane	30.0	1.53 (7)	0.01
Me	methylcyclohexane	40.0	5.26 (7)	0.01
Me	methylcyclohexane	45.0	9.15 (8)	0.01
Me	methylcyclohexane	49.0	13.8 (7)	0.01
Me	methylcyclohexane	49.0	13.5 (9)	0.001
Me	THF	49.0	18.9 (9)	0.01
Et	methylcyclohexane	28.0	3.6	0.008
Et	methylcyclohexane	35.0	9.8	0.011

[a] Numbers in parentheses are standard deviations in the least significant figure.

However, control experiments were required before intermolecular R–H elimination could be inferred from the results of these experiments. The fact that no isotopically mixed methanes were formed when the thermolysis of $Os(CO)_4(H)CH_3$ was carried out in the presence of an equivalent of CD_4 demonstrated that the isotopic content of methane (eq 10), once formed, was not disturbed by the

$$Os(CO)_4(H)CH_3 + CD_4 \rightarrow \text{only } CH_4 \text{ and } CD_4 \quad (10)$$

reaction. It proved impractical, however, to determine from the material remaining after partial reaction whether label exchange between $Os(CO)_4(H)CD_3$ and $Os(CO)_4(D)CH_3$ was occurring prior to elimination. Neither mass spectrometry nor ^1H NMR permitted determination of the isotopic nature of the hydride ligand associated with a particular methyl group; the parent ion in the mass spectrum of $Os(CO)_4(H)CH_3$ proved weak and H· loss facile, and the CH_3/H ^1H NMR coupling constant (^3J = 2.4 Hz)[5] was too small to be useful. Measurement of the extent of formation of $Os(CO)_4(D)CD_3$ and $Os(CO)_4(H)CH_3$ prior to elimination was thus impossible.

Fortunately some insight into the timing of the label crossover emerged from the study of the kinetics of these elimination reactions. Alkane loss was straightforwardly *first order* in $Os(CO)_4(H)R$ (eq 11), with k_1 in methyl-

$$-\frac{d[Os(CO)_4(H)R]}{dt} = k_1[Os(CO)_4(H)R] \text{ (in the absence of added nucleophile)} \quad (11)$$

cyclohexane being three times slower for R = methyl (from the data in Table I for $Os(CO)_4(H)CH_3$, k_1^{Me} at 28.0 °C could be extrapolated as $1.21 \times 10^{-5}\ s^{-1}$) than for R = ethyl ($k_1^{Et}$ at 28.0 °C was measured as $3.6 \times 10^{-5}\ s^{-1}$). The observed first-order rate constant k_1^{Me} showed no concentration dependence down to 10^{-3} M. The activation parameters obtained from the variable-temperature data (Table I) for $Os(CO)_4(H)CH_3$ were $\Delta H^* = 21.9$ (6) kcal/mol and $\Delta S^* = -8$ (2) eu.

Although the use of a donor solvent had no appreciable effect on the rate (as seen in Table I, k_1^{Me} increased by only a factor of 1.4 when THF was used as a solvent instead of methylcyclohexane), we decided to examine the reaction in the presence of more powerful nucleophiles.[8–18] Elim-

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(8) Nucleophilic acceleration of intramolecular reductive elimination has been predicted theoretically,[9] and there is evidence for its occurrence in a number of systems: added phosphines accelerate the formation of biaryls from *cis*-PtL_2Ar_2,[10] the formation of C_3H_7CN from *trans*-$PtH(C_3H_6CN)L_2$,[11] and the elimination of alkane from $Cp_2Zr(H)R$,[12] and it has been observed[10,13] that alkyl–acyl, alkyl–vinyl, and other eliminations in which an extra pair of electrons is available for coordination are generally faster than alkyl–alkyl eliminations. It is, however, much more common for intramolecular reductive elimination to be accelerated by oxidation,[14] coordination of an electron-withdrawing ligand,[15] or dissociation of a σ-donor ligand.[16] Nucleophilic acceleration would seem particularly unlikely with coordinatively saturated octahedral complexes such as $Os(CO)_4(H)R$, so it is not surprising that we have not observed it. It is worth noting that R–H elimination, although it sometimes requires prior ligand dissociation,[17] is more likely than R–R elimination to require no activation of any kind.[18]

Table II. First-Order Rate Constants for the Disappearance of *cis*-Os(CO)$_4$(H)R by Alkane Elimination According to Reaction 12 (Added PEt$_3$)[a]

R	T, °C	$10^5 k_2$,[b] s^{-1}	[PEt$_3$], M
Me	49.0	7.9 (2)[c]	0.07
Me	49.0	8.0 (2)[c]	0.2
Me	49.0	6.4 (1)	0.3
Et	28.0	2.28	1.5

[a] In methylcyclohexane. [b] Numbers in parentheses are the standard deviations in the least significant figure. [c] IR shows that about 10% of the reaction still proceeds according to reaction 1 under these conditions; thus the observed rate constant for disappearance of Os(CO)$_4$(H)R is slightly higher than it would be for reaction 12 alone.

ination of alkane still occurred, but, when a sufficiently large amount of a nucleophile L was present, Os(CO)$_4$L was formed by the loss of all alkyl and hydride ligands (eq 12).[5] (When only a few equivalents of L were present,

$$cis\text{-Os(CO)}_4\text{(H)R} + \text{excess PEt}_3 \xrightarrow[\text{methylcyclohexane}]{\Delta} \text{Os(CO)}_4\text{(PEt}_3\text{)} + \text{R–H} \quad (12)$$

$$\text{R = Me, 49 °C; R = Et, 28 °C}$$

reaction 1 continued to occur as well.) In contrast to reaction 1, however, labeling experiments (reaction 13)

$$\text{Os(CO)}_4\text{(H)CD}_3 + \text{Os(CO)}_4\text{(D)CH}_3 \xrightarrow[\text{49 °C, methylcyclohexane}]{\text{110 equiv of PEt}_3} \text{no CD}_4 \quad (13)$$

showed that this reaction was intramolecular. Furthermore, added ^{13}CO was incorporated neither into the product nor into starting material recovered after partial reaction (eq 14)—thus ruling out dissociation and recoordination of CO during the reaction.

$$\text{Os(CO)}_4\text{(H)CH}_3 \xrightarrow[\text{42 h, 25 °C, methylcyclohexane}]{^{13}\text{CO, PEt}_3} \text{Os(CO)}_4\text{(PEt}_3\text{) and unreacted Os(CO)}_4\text{(H)CH}_3\text{, both containing only natural abundance }^{13}\text{CO} \quad (14)$$

A similar experiment (eq 15) (carrying out the reaction under ^{13}CO, stopping it short of completion, and checking both product and recovered starting material for ^{13}CO incorporation) showed that dissociation and recoordination of CO did not occur during reaction 1.

$$\text{Os(CO)}_4\text{(H)CH}_3 \xrightarrow[\text{24 h, 25 °C, methylcyclohexane}]{^{13}\text{CO}} \text{(OC)}_4\text{HOs—OsCH}_3\text{(CO)}_4 \text{ and unreacted Os(CO)}_4\text{(H)CH}_3\text{, both containing only natural abundance }^{13}\text{CO} \quad (15)$$

As shown in Table II, the rate of reaction 12 proved first order in Os(CO)$_4$(H)R and zero order in PEt$_3$ (eq 16). (The slightly higher values of k_2^{Me} seen

$$-\frac{d[\text{Os(CO)}_4\text{(H)R}]}{dt} = k_2[\text{Os(CO)}_4\text{(H)R}] \text{ in the presence of sufficient added nucleophile} \quad (16)$$

in Table II at the lower concentrations of PEt$_3$ reflect the fact that about 10% of the Os(CO)$_4$(H)R still disappears by reaction 1 under these conditions.) Furthermore, k_1^{Me} is almost exactly twice k_2^{Me} in methylcyclohexane at 49 °C, and k_1^{Et} is approximately twice k_2^{Et} in methylcyclohexane at 28 °C.

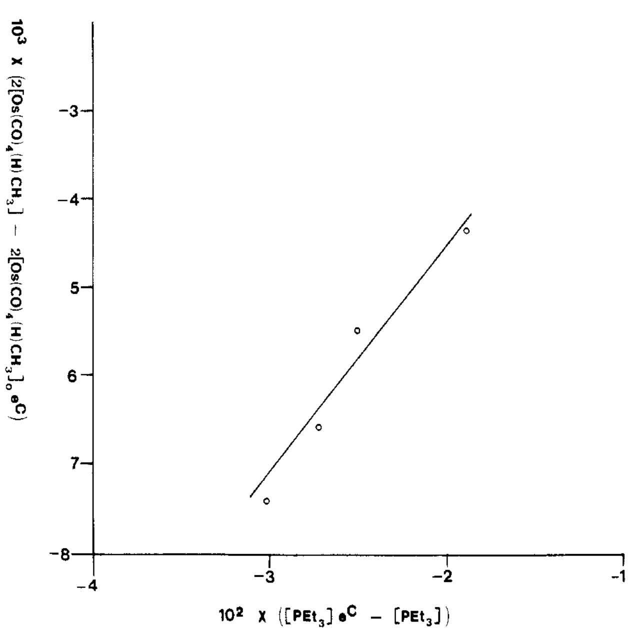

Figure 1. Plot of $2[\text{Os(CO)}_4\text{(H)CH}_3] - 2[\text{Os(CO)}_4\text{(H)CH}_3]_0 e^C$ vs. $[\text{PEt}_3]e^C - [\text{PEt}_3]$, where C is a function of time defined below eq 20, for methane elimination from Os(CO)$_4$(H)CH$_3$ with $[\text{Os(CO)}_4\text{(H)CH}_3]_0$ = 0.030 M and [PEt$_3$] = 0.17 M at 49.0 °C in methylcyclohexane.

The observation that k_1 was twice k_2 suggested the mechanism in Scheme I, with an intermediate X formed from Os(CO)$_4$(H)R at a rate k_2 (the rate-determining step for the overall reaction) and reacting rapidly with either an additional equivalent of Os(CO)$_4$(H)R (rate k_3) or the nucleophile L (rate k_4). This scheme implies that (1) if sufficient L is present, the reaction occurs entirely by the k_4 path and the net rate of disappearance of Os(CO)$_4$(H)R is just k_2, (2) if no L is present, the reaction occurs entirely by the k_3 path and the net rate of disappearance of Os(CO)$_4$(H)R is $2k_2$, and (3) if a low concentration of L is present, a mixture of products will result as $k_3[\text{Os(CO)}_4\text{(H)R}]$ and $k_4[\text{L}]$ compete. In case 3 (low [L]), the disappearance of Os(CO)$_4$(H)R should not show first-order behavior; the rate of its disappearance should decrease during the reaction and approach k_2 as the $[\text{Os(CO)}_4\text{(H)R}]/[\text{L}]$ ratio approaches zero.

Scheme I

$$\text{Os(CO)}_4\text{(H)R} \xrightarrow[\text{rate determing}]{k_2} \text{X} \quad (17)$$

$$\text{X} + \text{Os(CO)}_4\text{(H)R} \xrightarrow[\text{fast}]{k_3} \text{(OC)}_4\text{HOs-OsR(CO)}_4 + \text{R-H} \quad (18)$$

$$\text{X} + \text{L} \xrightarrow[\text{fast}]{k_4} \text{Os(CO)}_4\text{L} + \text{R-H} \quad (19)$$

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Table III. Relative Reactivities of Various Nucleophiles and $Os(CO)_4(H)CH_3$ toward the Reactive Intermediate in Reactions 1 and 12 (Methane Elimination)[a]

nucleophile (M)	k_4/k_3[b,c]	nucleophile (M)	k_4/k_3[b,c]
$P(C_2H_5)_3$ (0.17)	0.35 (3)	$P(OCH_3)_3$ (0.43)	0.050 (6)
PPh_3 (0.21)	0.15 (3)	pyridine (≥0.74)	<0.02

[a] At 49.0 °C in methylcyclohexane. [b] As defined in Scheme I. [c] Numbers in parentheses are the standard deviations in the least significant figure.

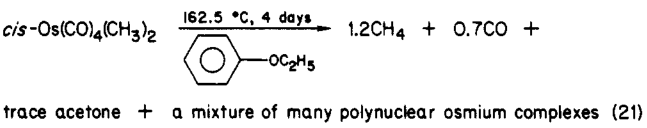
Scheme I was tested by careful determination of $[Os(CO)_4(H)CH_3]$ as a function of time in the presence of modest amounts of PEt_3 and other nucleophiles L. The resulting data fit eq 20 quite well, where C is defined as

$$2[Os(CO)_4(H)CH_3]_t - 2[Os(CO)_4(H)CH_3]_0 e^C = \frac{k_4}{k_3}([L]e^C - [L]) \quad (20)$$

$2k_2t + 2 \ln ([Os(CO)_4(H)CH_3]_t/[Os(CO)_4(H)CH_3]_0)$. (As shown in detail in Appendix A, a steady-state approximation in [X] allows derivation of eq 20 as the integrated form of the rate law corresponding to Scheme I.) As seen in Figure 1 for L = PEt_3, a plot of $2[Os(CO)_4(H)CH_3]_t - 2[Os(CO)_4(H)CH_3]_0e^C$ vs. $[L]e^C - [L]$ gave a straight line with an intercept of zero as required; its slope, k_4/k_3, showed the relative reactivity of Et_3P and $Os(CO)_4(H)CH_3$ toward the intermediate X. Values of k_4/k_3 for a variety of nucleophiles L, obtained from such plots and given in Table III, show that even PEt_3 is not as reactive toward X as is $Os(CO)_4(H)CH_3$.

The validity of Scheme I means that reactions 1 and 12 proceed through a common intermediate X. The absence of crossover in reaction 13, which shows that reaction 12 is intramolecular, thus demonstrates that the formation of X is intramolecular in reaction 1 as well as in reaction 12. The crossover observed in reactions 8 and 9 must therefore occur at the time of alkane elimination and not before, and reaction 1 is therefore intermolecular. (It is logically possible, although we consider it unlikely, for label crossover to occur prior to reaction 1 rather than during it; some unknown species, not present in reaction 13, would have to catalyze the exchange of methyl or hydride ligands in reaction 1 prior to elimination.[19])

The Elimination of Methane from *cis*-$Os(CO)_4(CH_3)_2$. The absence of ethane as a product of the thermal decomposition of *cis*-$Os(CO)_4(CH_3)_2$ (eq 21) implied that,



(21)

as with *cis*-$Os(CO)_4(H)CH_3$, $Os(CO)_4$ was not formed by simple intramolecular reductive elimination. In contrast to *cis*-$Os(CO)_4(H)R$, *cis*-$Os(CO)_4Me_2$ proved very stable: after 4 days at 162.5 °C in *n*-dodecane solution 80% of it was recovered unchanged. The fact that more than 1 equiv of methane was formed in reaction 21 implied, and reaction

Table IV. Isotopic Composition of Methanes Formed upon Thermolysis of *cis*-$Os(CO)_4(CD_3)_2$ in Various Solvents[a]

solvent	$[Os(CO)_4(CD_3)_2]_0$, M	CD_4/CD_3H
n-dodecane	0.30	0.90
n-dodecane	0.056	0.24
di-*n*-pentyl ether	0.056	0.18
phenetole	0.052	0.050
phenetole	0.065	0.069
sec-butylbenzene	0.055	0.077
2-octanone	0.059	0.025
acetophenone	0.051	0.022
1,2,3,4-tetramethylbenzene	0.080	0.57
1,2,3,4-tetramethylbenzene	0.043	0.19

[a] For 3 days at 164 ± 1 °C.

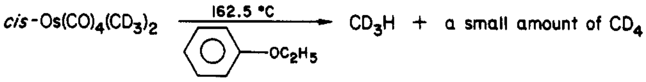
Table V. CD_4/CD_3H Ratios from the Partial Thermolysis of $Os(CO)_4(CD_3)_2$ in Mixtures of *n*-$C_{12}H_{26}$ and *n*-$C_{12}D_{26}$[a]

$[CD_4]/[CD_3H]$	y(mole fraction of $C_{12}H_{26}$)
1.10	0.5
1.60	0.263
1.35	0.40
1.75	0.225
1.90	0.163

[a] 0.092 M $Os(CO)_4(CD_3)_2$, 162.5 °C, 4 days, 20% decomposition.

23[20] confirmed, that most methane molecules contained one hydrogen from the solvent.

$$[Os(CO)_4]^{2-} + CD_3OTs \rightarrow cis\text{-}Os(CO)_4(CD_3)_2 \quad (22)$$



(23)

Even methane gas was attacked when the thermolysis of this volatile compound was carried out in a closed bulb without solvent (reaction 24). (Methane was not attacked

$$cis\text{-}Os(CO)_4(CH_3)_2 + CD_4 \xrightarrow{162.5\ °C} \text{some } CD_3H \quad (24)$$

in presence of solvent: thermolysis of $Os(CO)_4(CH_3)_2$ in *n*-dodecane at 162.5 °C in the presence of CD_4 produced only CH_4 and CD_4). The formation of methane was, however, irreversible under these conditions: the amount of $Os(CO)_4(CH_3)_2$ remaining after a given thermolysis time was unaffected by the presence of 0.2 atm of CH_4, and no decrease in the deuterium content was found in $Os(CO)_4(CD_3)_2$ recovered after partial reaction in the presence of 1 equiv of CH_4.

These results suggested the formation of an intermediate Y capable of generating methane by hydrogen abstraction from solvent or (in the absence of solvent) from methane itself. However, thermolysis of $Os(CO)_4(CD_3)_2$ in a variety of solvents (Table IV) showed that some CD_4 was always formed regardless of solvent and dilution—and thus arose entirely from the CD_3 ligands and not from solvent attack. Determination of the origin of this CD_3-ligand-derived CD_4 was made difficult by our discovery that, at least in the gas phase, slow methyl group exchange between molecules occurred prior to methane elimination (reaction 25).[21] We

$$cis\text{-}Os(CO)_4(CH_3)_2 + cis\text{-}Os(CO)_4(^{13}CH_3)_2 \rightarrow Os(CO)_4(CH_3)_2 \text{ and } Os(CO)_4(^{13}CH_3)_2 \text{ plus some } Os(CO)_4(^{13}CH_3)(CH_3) \quad (25)$$

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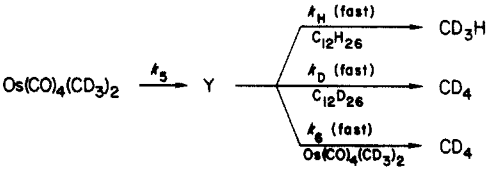
[19] Prof. R. G. Bergman has pointed out that the added Et_3P in reaction 13 might make methane elimination intramolecular by suppressing the operation of such a catalyst (which would otherwise exchange methyl or hydride ligands among molecules of the hydrido methyl complex and which would thus produce *apparent* intermolecular methane elimination in reaction 1, without Et_3P). The existence of a catalyst capable of scrambling methyl or hydrige ligands among molecules of a coordinatively saturated octahedral complex at 49 °C seems extremely unlikely, and the presence of such a catalyst under the high-vacuum-line conditions of these experiments seems even more improbable.

[20] $Os(CO)_4(CD_3)_2$ was used because CD_4 and CD_3H can be more accurately determined by mass spectrometry than CH_3D and CH_4.

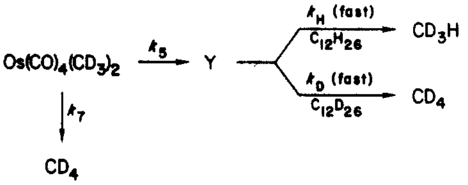
Scheme II



$$\frac{[CD_4]}{[CD_3H]} = \frac{k_D}{k_H}\,\frac{1-y}{y} + \frac{R}{y} \qquad (26)$$

y = mole fraction $C_{12}H_{26}$ in solvent
R = CD_4/CD_3H ratio in pure $C_{12}H_{26}$

Scheme III



$$\frac{[CD_4]}{[CD_3H]} = \frac{k_D}{k_H}\,\frac{1-y}{y}\,(1+R) + R \qquad (27)$$

therefore turned our attention back to the other methane-forming intermediate Y and attempted to establish its identity by determining its selectivity for H vs. D abstraction from solvent. (The attempted use of more efficient hydrogen sources, e.g., thiols as radical traps, gave a variety of byproducts at temperatures far below those required for the generation of methane.)

We therefore carried out the thermal decomposition of $Os(CO)_4(CD_3)_2$ in a series of mixtures of n-$C_{12}D_{26}$ and n-$C_{12}H_{26}$ and measured the CD_4/CD_3H ratio of the methane evolved (Table V). By carrying out the reaction for a constant period of time to low conversion, with a constant initial concentration of $Os(CO)_4(CD_3)_2$, the concentration of $Os(CO)_4(CD_3)_2$ was kept effectively constant. The resulting data were then fit[22a] to eq 26 and 27 (the derivations of which are given in Appendix B), arising from the two plausible reaction mechanisms,[22b] Schemes II and III.

In Scheme II, the CD_3-ligand-derived CD_4 is formed by attack on $Os(CO)_4(CD_3)_2$ by the same intermediate Y which attacks solvent; in Scheme III, the CD_3-ligand-derived CD_4 is formed by a separate reaction, rate constant k_7, which does not involve the intermediate Y. (The statement in our preliminary communication[2c] that the slope of a plot of CD_4/CD_3H vs. $[C_{12}D_{26}]/[C_{12}H_{26}]$ is k_H/k_D is incorrect.[23,24])

Agreement with eq 26 could only be obtained for negative values of k_D/k_H, demonstrating that the mechanism of Scheme II was not producing the majority of the methane. Agreement with eq 27 was substantially better, although repeated experimental measurements of R (the CD_4/CD_3H ratio in pure $C_{12}H_{26}$) ranged from 0.65 to 0.82 and limited the accuracy with which k_D/k_H could be determined. The average value of R, 0.76, gave k_D/k_H as 0.148 ± 0.013 and k_H/k_D as 6.8 ± 0.6. As the lowest measured value of R, 0.65, gave k_H/k_D as 5.7 ± 0.5, it seems safe to conclude that k_H/k_D is at least 5 for solvent attack by the intermediate Y.

The Elimination of Ethane and Ethylene from *cis*-$Os(CO)_4(C_2H_5)_2$. Preliminary work in our group (John Evans, 1974) had shown that the only organic products of the thermal decomposition of *cis*-$Os(CO)_4(C_2H_5)_2$ were ethylene and ethane, with a C_2H_4/C_2H_6 mole ratio of 0.6. In view of the intermolecular nature of reaction 1 (R–H elimination from $Os(CO)_4(H)R$), we decided to investigate the possibility that $Os(CO)_4(C_2H_5)_2$ also gave ethane by an intermolecular process—in contrast to the intramolecular formation of alkene and alkane found for most dialkyl complexes containing β-hydrogens (e.g., *cis*-$(Ph_3P)_2Pt(n\text{-}Bu)_2$[25]). Thermolysis of a 1:1 mixture of $Os(CO)_4(C_2H_5)_2$ and $Os(CO)_4(C_2D_5)_2$ (eq 28 and 29), how-

$$[Os(CO)_4]^{2-} \xrightarrow[51\ ^\circ C,\ \text{tetraglyme}]{C_2D_5OTs} cis\text{-}Os(CO)_4(C_2D_5)_2 \qquad (28)$$

$$cis\text{-}Os(CO)_4(C_2D_5)_2 + cis\text{-}Os(CO)_4(C_2H_5)_2 \xrightarrow[n\text{-octane}]{72\ h,\ 126\ ^\circ C} C_2H_4 + C_2D_4 + C_2H_3D + C_2HD_3 + CH_2{=}CD_2 + cis\text{-}CHD{=}CHD + trans\text{-}CHD{=}CHD \qquad (29)$$

ever, gave ethylene in which all possible H/D isomers could be identified by their characteristic gas-phase IR spectra.[26] This label scrambling—presumably the result of a reversible β-hydrogen elimination—precluded determination of the intra- or intermolecularity of ethane elimination.

Discussion and Additional Results in Related Systems

Nature of the Intermediate in R–H Elimination from *cis*-$Os(CO)_4(H)R$. The only plausible identity for the intermediate X in Scheme I is that of an acyl hydride. The negative $\Delta S^\ddagger$ does not suggest carbonyl dissociation, and this reaction occurs far below the temperature (about 125 °C) normally required for carbonyl dissociation from an $Os(CO)_4$ unit.[27,28] The fact that $Os(CO)_4L$ can be formed from X without incorporation of external ^{13}CO confirms that X retains all four carbonyls from *cis*-$Os(CO)_4(H)R$. As X obviously also retains the alkyl and hydride ligands of *cis*-$Os(CO)_4(H)R$, and as the rate of formation of X is largely solvent-independent, X must be an *isomer* of *cis*-$Os(CO)_4(H)R$ capable of rapid reaction with either a phosphine or the unisomerized alkyl hydride complex.

There is no plausible reason why the hypothetical *trans*-$Os(CO)_4(H)R$ should possess such enhanced reactivity. Among the other possible isomers of $Os(CO)_4$-

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[21] It seems likely that this occurs by recombination (permitted by the low concentration of hydrogen atom donors in the gas phase) of methyl radicals formed by Os–CH_3 bond homolysis.

[22] (a) Curve fitting was done by the nonlinear regression program BMDP3R, CDC version, as released August 1983 by Vogelback Computing Center, Northwestern University. The dependent variable was CD_4/CD_3H and the independent variable y; the parameters were R and k_D/k_H. (b) We assume Y is sufficiently reactive that the generation of free Y is effectively irreversible; reversible formation of two reactive fragments (i.e., radicals) within a solvent cage may precede the formation of free Y.

[23] Our original approach was suggested by that of Pryor and coworkers[24] to the measurement of the selectivity of methyl radicals for t-BuSD vs. various hydrocarbons, given the presence of some protio impurity in the former. The ratio $k_{SH}[t\text{-BuSH}]/k_{SD}[t\text{-BuSD}]$ is constant, *at least for a given batch of t-BuSD*, and a plot of CH_4/CH_3D vs. [hydrocarbon]/[deuterated mercaptan] would therefore have a slope of k(hydrocarbon)/k_{SD}. In our case $k_6[Os(CO)_4(CD_3)_2]_0/k_H[C_{12}H_{26}]$ is not constant as the $C_{12}D_{26}/C_{12}H_{26}$ ratio varies, and CD_4/CD_3H should not be a linear function of $[C_{12}D_{26}]/[C_{12}H_{26}]$ but rather one of the type described in eq 26 or 27. We thank Prof. R. G. Bergman for bringing this point to our attention.

[24] Pryor, W. A.; Fuller, D. L.; Stankey, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 1632.

[25] Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258.

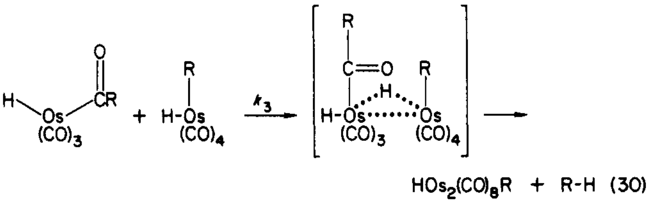
[26] (a) Rochkind, M. M. *Anal. Chem.* **1968**, *40*, 762. (b) Golike, R. C.; Mills, M.; Person, W. B.; Crawford, B., Jr. *J. Chem. Phys.* **1957**, *25*, 1266. (c) Lehmann, W. *J. Mol. Spectrosc.* **1961**, *7*, 1.

[27] The rate of dissociative CO exchange per $Os(CO)_4$ unit in $Os_3(CO)_{12}$[28] extrapolates to 25 × 10^{-5} s^{-1} at 125.8 °C. The rate of CO loss from the $Os(CO)_4$ unit in $Os(CO)_4H_2$ is 6 × 10^{-5} s^{-1} at that temperature.[2a]

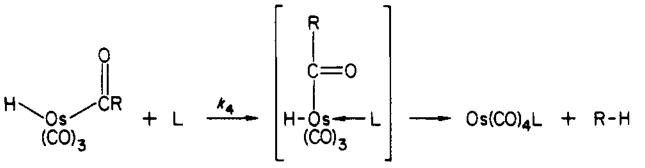
[28] Cetini, G.; Gambino, O.; Sappa, E.; Vaglio, G. A. *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat.* **1967**, *101*, 855.

(H)R, a five-coordinate alkyl formyl complex $Os(CO)_3(R)CHO$ can be ruled out on two grounds: (1) it should be much higher in energy than the corresponding acyl hydride;[29-35] (2) its formation from a hydrido carbonyl should have occurred with a substantial kinetic isotope effect (a k_H/k_D of 2.8 has been reported for the carbonylation of $(\eta^5\text{-}C_5Me_5)_2Th(R)$ (H or D)[34]), whereas reactions 8 and 9 show a k_H/k_D of 1.1.[36]

The identification of X as an unsolvated acyl hydride implies from Scheme I that reactions 30 and 31 are possible. The fact that $k_3 \approx k_4$ for nucleophilic phosphines (Table III) implies that M–H is behaving as a nucleophile and suggests the intermediate drawn in eq 30, with a three-center, two-electron bond.[37] (It has become widely recognized that transition-metal hydrides are excellent donor ligands, and this property has recently found considerable use in the synthesis of hydride-bridged dimers.[38])

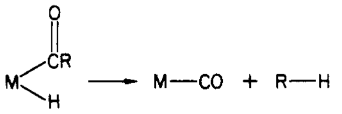


(30)



(31)

The fact that no external ^{13}CO is incorporated into either of the final products implies that the final alkane elimination must occur without CO dissociation, i.e., by the direct elimination of alkane from an acyl hydride as shown in eq 32. This step seems implausible if one thinks of it as proceeding via initial migration of R onto the metal; a discrete alkyl carbonyl hydride intermediate (such as $Os(CO)_4(H)(R)L$) would violate the 18-electron rule. However, reaction 32 becomes much more plausible if one thinks of it as an alkyl migration directly onto the hydride ligand; for that matter, the distinction between migration onto the metal and onto the hydride may be more semantic than real.



(32)

The literature does not offer much evidence for or against direct alkane elimination from acyl hydrides by reactions like (32). Hydrido formyl complexes are known to give the corresponding carbonyls by H_2 loss, but it is unclear whether or not there is prior dissociation of another ligand;[39] chelation-stabilized acyl hydrides are probably reluctant to undergo C–H elimination and carbonyl complex formation by *any* mechanism;[40] other acyl hydrides[41] have sometimes been reported to undergo alkane elimination and/or carbonyl complex formation, but there has frequently been evidence suggesting prior ligand dissociation (e.g., loss of PMe_3 from $ClRh(PMe_3)_3(H)C(O)R$[41d]). Apparent formation of $Fe(dmpe)_2CO$ from *cis*-$HFe(C(O)C_2H_5)(dmpe)_2$ has been reported in solution at room temperature—conditions under which dissociation of one end of a dmpe ($Me_2PCH_2CH_2PMe_2$) ligand would seem unlikely. Processes like reaction 32 are also suggested (but certainly not proven) by the formation of methane in reaction 33[42] and in reaction 34[43] and by the facile decarbonylation reported for a ruthenium bis(aldehyde) complex under conditions where coordinative unsaturation is ex-

$$\textit{trans}\text{-}ClNi(PMe_3)_2C(=O)CH_3 + [Me_3PH]^+Cl^- \rightarrow (Me_3P)_3NiCl_2 + CO + CH_4 \quad (33)$$

$$[CpCo(PMe_3)_2C(=O)CH_3]^+ \xrightarrow[\text{THF}]{\text{NaH}} CpCo(CO)PMe_3 + CH_4 + PMe_3 \quad (34)$$

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(29) Dedieu and Nakamura[30] have concluded from LCAO–MO–SCF calculations that $Fe(CO)_4(H)C(O)CH_3$ is 12.6 kcal/mol more stable than $Fe(CO)_4(CH_3)CHO$, and they have summarized the considerable experimental evidence[31-35] than an $M(H)CO \rightleftharpoons M\text{–}CHO$ equilibrium will in general lie farther to the left than the corresponding $M(R)CO \rightleftharpoons M\text{–}C(O)R$ equilibrium. The magnitude of the rate measured[34] for $(C_5Me_5)_2Th(OR)H + CO \rightarrow (C_5Me_5)_2Th(OR)CHO$ suggests, however, that the formation of a formyl complex from a hydrido carbonyl may be very rapid even when the reaction is thermodynamically unfavorable.

(30) Dedieu, A.; Nakamura, S. *J. Organomet. Chem.* **1984**, *260*, C63.

(31) Casey, C. P.; Neumann, S. M.; Andrews, M. A.; McAlister, D. R. *Pure Appl. Chem.* **1980**, *52*, 625–633.

(32) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1–38.

(33) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946.

(34) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051.

(35) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166.

(36) As explained near the beginning of the Results, these k_H/k_D values are derived (after correction for the relative amounts of H and D in the starting materials) from the R_DH/R_DD ratios in reactions 8 and 9. If one assumes that the protioformyl ($Os(CO)_3(R)CHO$ = XH) and the deuterioformyl ($Os(CO)_3(R)CDO$ = XD) somehow generate R_D–H and R_D–D with equal bimolecular rate constants from the perdeuterioalkyl ligand R_D or $Os(CO)_4(H)R_D$, these R_DH/R_DD ratios reflect the relative rates at which XH and XD are formed, and the derived k_H/k_D values are those for the formation of XH and XD. Although some such mechanistic assumption is required in order to deduce isotope effects for particular steps from the results of reactions 8 and 9, the nearly random product H/D distribution suggests that there is no appreciable kinetic or thermodynamic isotope effect anywhere.

(37) Humphries and Kaesz (Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145) have written a structure for the intermediate in reaction 30 in which the Os–H bond of $Os(CO)_4(H)R$ has been broken by complete addition across the osmium of the acyl complex. Insofar as this proposal implies that the incoming hydride becomes equivalent to the hydride already present (on the acyl osmium), it can be dismissed as unlikely; the CD_4/CD_3H ratio observed would require a substantial inverse isotope effect. One cannot, however, rule out the possibility of some hydride exchange within the intermediate, and in fact one cannot be certain that the alkyl group eliminated is from the acyl ligand as assumed.

(38) See: Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 51 and references therein. Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 514 and references therein. Richmond, T. G.; Basolo, F.; Shriver, D. F. *Organometallics* **1982**, *1*, 1624. Other recent examples include (a) $HCr_2(CO)_{10}^-$ from $HCr(CO)_5^-$: Darensbourg, M. Y.; Bau, R.; Marks, M. W.; Burch, R. R., Jr.; Deaton, J. C.; Slater, S. *J. Am. Chem. Soc.* **1982**, *104*, 6961. (b) $HFeM(CO)_9^-$ from $HFe(CO)_4^-$: Arndt, L.; Delord, T.; Darensbourg, M. Y. *Ibid.* **1984**, *106*, 456. (c) $Cp_2MM'(NO)_4H^+$ from $CpM(NO)_2H$: Hames, B. W.; Legzdins, P. *Organometallics* **1982**, *1*, 116. (d) $Cp_2Mo_2(CO)_6H^+$ from $CpMo(CO)_3H$: Beck, W.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214. (e) $Cp_2Nb(CO)(\mu\text{-}H)Nb(CO)_3Cp$ from $Cp_2Nb(CO)H$: Herrmann, W. A.; Biersack, H.; Balbach, B.; Wülknitz, P.; Ziegler, M. L. *Chem. Ber.* **1984**, *117*, 79. (f) $Cp_2Ta(CO)(\mu\text{-}H)M(CO)_5$ from $Cp_2Ta(CO)H$: Leblanc, J. C.; Reynoud, J. F.; Moise, C. *J. Organomet. Chem.* **1983**, *244*, C24.

(39) (a) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503. (b) Thorn, D. L. *Organometallics* **1982**, *1*, 197. The subject has been reviewed in ref 32.

(40) (a) Suggs, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 640. (b) Landvatter, E. F.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 506.

(41) (a) Francis, B. R.; Green, M. L. H.; Luong-thi, T.; Moser, G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1339. (b) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, C7. (c) Milstein, D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3773. (d) Milstein, D. *Organometallics* **1982**, *1*, 1549; *J. Chem. Soc., Chem. Commun.* **1982**, 1357. (e) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.

(42) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2524.

Scheme IV

$$\textit{cis}\text{-Os(CO)}_4\text{(H)CH}_3 + \textit{cis}\text{-Os(CO)}_4\text{H}_2 \longrightarrow \text{H}_2\text{Os}_2\text{(CO)}_8 + \text{CH}_4 \quad (35)$$

$$\textit{cis}\text{-Os(CO)}_4\text{(H)CH}_3 + \text{HRe(CO)}_5 \longrightarrow \text{HOs(CO)}_4\text{Re(CO)}_5 + \text{CH}_4 \quad (36)$$

$$\textit{cis}\text{-Os(CO)}_4\text{(CH}_3\text{)}_2 + \textit{cis}\text{-Os(CO)}_4\text{H}_2 \longrightarrow \text{HOs}_2\text{(CO)}_8\text{CH}_3 + \text{CH}_4 \quad (37)$$

$$\textit{cis}\text{-Os(CO)}_4\text{(CH}_3\text{)}_2 + \text{excess } \textit{cis}\text{-Os(CO)}_4\text{(H)CH}_3 \longrightarrow$$
$$\text{some (OC)}_4\text{CH}_3\text{Os-OsCH}_3\text{(CO)}_4 \text{ as well as (OC)}_4\text{HOs-OsCH}_3\text{(CO)}_4 \quad (38)$$

tremely unlikely.[44] Further investigation of such systems is clearly desirable.

We have been able to confirm that the proposed intermolecular alkane elimination between a hydride and a coordinatively unsaturated acyl (reaction 30) can occur in other systems. We have already reported[5] the synthetic use of alkyl and hydride complexes other than $Os(CO)_4(H)R$ in reactions like (1) and (30) (Scheme IV). Methane is also formed when other coordinatively unsaturated acetyl complexes (e.g., $RhI_3(CO)Ac^-$,[45] $Ir(CO)Cl_2(AsPh_3)Ac$[46]) react with *cis*-$Os(CO)_4H_2$ (eq 39).

$$[\text{RhI}_3\text{(CO)C(=O)CH}_3]^- + \text{Os(CO)}_4\text{H}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{49\ ^\circ\text{C}} \text{CH}_4\text{(1 equiv)} + \text{some CH}_3\text{CHO} \quad (39)$$

Reaction 39 does not involve proton transfer, as demonstrated by the fact that treatment of $RhI_3(CO)Ac^-$ with CF_3CO_2H does not give methane. Reaction 40 proceeds

$$\text{IrCl}_2\text{(AsPh}_3\text{)(CO)}_2\text{CH}_3 + \text{Os(CO)}_4\text{H}_2 \xrightarrow{49\,^\circ\text{C}} 1 \text{ equiv of CH}_4 \quad (40)$$

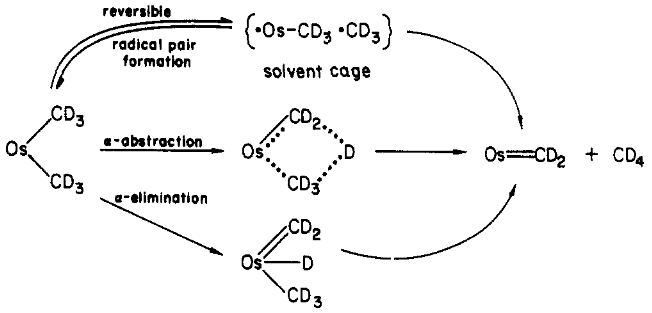
through the known[46] five-coordinate acyl $Ir(CO)Cl_2(AsPh_3)C(O)CH_3$, according to the mechanism of reactions 41 and 42; at 49 °C in chlorobenzene, the observed first-order rate constants for the disappearance of $IrCl_2(AsPh_3)(CO)_2CH_3$ ($4.2\ (4) \times 10^{-5}\ s^{-1}$) and for the disappearance of an equivalent of $Os(CO)_4H_2$ when the latter is present in excess ($4.7\ (7) \times 10^{-5}\ s^{-1}$) agree well with the literature value of k_8 ($5.1 \times 10^{-5}\ s^{-1}$) determined from kinetic studies of acetyl complex formation in the presence of a variety of added ligands.[46]

$$\text{IrCl}_2\text{(AsPh}_3\text{)(CO)}_2\text{CH}_3 \xrightarrow{k_8} \text{Ir(CO)Cl}_2\text{(AsPh}_3\text{)C(=O)CH}_3 \quad (41)$$

$$\text{Ir(CO)Cl}_2\text{(AsPh}_3\text{)C(=O)CH}_3 + \text{Os(CO)}_4\text{H}_2 \xrightarrow{\text{fast}} \text{CH}_4 \quad (42)$$

Nature of the Intermediate in Methane Elimination from *cis*-$Os(CO)_4(CH_3)_2$. If we conclude that Scheme III is the principal decomposition pathway for $Os(CO)_4(CD_3)_2$, as it apparently is under the conditions used to obtain the data in Table V, we must identify intermediate Y. The isotope effect for solvent attack is compatible with that expected for a methyl radical at 162.5 °C (k_H/k_D from 5.2[47,49] to 5.6[48,49]) and significantly larger than that (1.38) reported[50] for attack on cyclohexane/cyclohexane-d_{12} by the species generated upon photolysis of solutions of $(C_5Me_5)Ir(PMe_3)H_2$. Although it thus seems likely that Y is a methyl radical, one cannot rule out the possibility that it is a methyl- or acetylosmium complex generated slowly at 162.5 °C and capable of C–H bond activation with an unusually high kinetic isotope effect. A number of attempts to observe CIDNP in this system have failed.

Scheme V



The remaining question is the nature of the path in Scheme III (rate constant k_7) which leads to CD_4 without involving Y. If Y is a *free* methyl ($\cdot CD_3$) radical, the k_7 path may be the formation of CD_4 from a solvent cage containing $\cdot CD_3$ and $\cdot Os(CO)_4CD_3$; the k_7 path may also be either of two closely related nonradical reactions, α-hydrogen abstraction and α-hydrogen elimination.[51] (All of these possibilities are illustrated in Scheme V.) However, the increase in the CD_4/CD_3H ratio at higher initial $Os(CO)_4(CD_3)_2$ concentrations—seen in the data in Table IV for several solvents—suggests that some CD_4 also arises from $\cdot CD_3$ attack on $Os(CO)_4(CD_3)_2$[52] (a k_6 path) at high concentrations of the latter. Under the conditions of Table IV the thermolysis of $Os(CO)_4(CD_3)_2$ may thus involve a Scheme II mechanism as well as a Scheme III one.

The $Os(CO)_4(CH_3)_2$ system thus resembles one (the thermolysis of *trans*-$PtIMe(PR_3)_2$) recently investigated by Turco and Morvillo.[53] By similar techniques (thermal decomposition in mixtures of ethylbenzene-d_0 and ethylbenzene-d_{10}, solvent and concentration dependence of solvent attack) these workers have shown that the main route to methane formation from *trans*-$PtIMe(PR_3)_2$ at 120 °C is homolysis of the Pt–CH_3 bond and formation of methyl radicals, which then form methane by abstraction of hydrogen from solvent or from phosphine alkyl groups; a minor route to methane involves two coordinated methyl groups (α-elimination or α-abstraction).

It is interesting to compare our $Os(CO)_4(CH_3)_2$ results with those obtained by Poliakoff, Turner, and co-workers[54] in the gas phase by IR laser pyrolysis (with SF_6 as a chemically inert photosensitizer) in the presence of 0.2 atm of CO and with those obtained by L'Eplattenier and Pelichet[55] at 120 °C in solution under 120 atm of CO. In both cases $Os(CO)_5$ was the only product identified, reflecting the presence of CO/Os ratios far higher than those used in our experiments.

Summary

The most significant result in all of these studies is the absence of simple intramolecular reductive elimination

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(44) Rauchfuss, T. B. *J. Am. Chem. Soc.* **1979**, *101*, 1045.

(45) Forster, D. *J. Am. Chem. Soc.* **1976**, *98*, 846.

(46) Glyde, R. W.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 331.

(47) The extrapolated selectivity[49] for $\cdot CD_3$ attack on secondary H and D in propane is $k_H/k_D = 5.2$: Jackson, W. M.; McNesby, J. R.; Darwent, B. DeB. *J. Chem. Phys.* **1962**, *37*, 1610.

(48) The extrapolated selectivity[49] for $\cdot CH_3$ or $\cdot CD_3$ attack on mixtures of C_2H_6 and C_2D_6 is $k_H/k_D = 5.6$: McNesby, J. R. *J. Phys. Chem.* **1962**, *64*, 1671 and references therein.

(49) Such isotope effects are known to be almost identical whether the reaction is conducted in solution or in the gas phase: Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966; p 163.

(50) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(51) For definitions see: McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629.

(52) Organometallic derivatives of $Os(CO)_4(CD_3)_2$, formed during these prolonged reactions, may also be a source of D·, and therefore of CD_4, at these concentrations.

(53) Morvillo, A.; Turco, A. *J. Organomet. Chem.* **1983**, *258*, 383.

(54) Bristow, N. J.; Moore, B. D.; Poliakoff, M.; Ryott, G. J.; Turner, J. J. *J. Organomet. Chem.* **1984**, *260*, 181.

(55) L'Eplattenier, F.; Pelichet, C. *Helv. Chim. Acta* **1970**, *53*, 1091.

(reaction 43) in all cases, including $Os(CO)_4H_2$.[2a]

$$Os(CO)_4RR' \nrightarrow Os(CO)_4 + R\text{–}R' \qquad (43)$$

We believe that this result reflects the high energy of $Os(CO)_4$ and the strength of the bonds it can form to hydrogen and carbon. The spin state of $Os(CO)_4$ may also be relevant; the ground state of $Fe(CO)_4$ is a triplet,[56] and that of $Os(CO)_4$ may be also, suggesting that the (presumably singlet) initial product of reaction 40 may be an excited state of $Os(CO)_4$. Such arguments have led Veillard and Dedieu[57] to pronounce the elimination of H_2 from $Fe(CO)_4H_2$ thermally forbidden (despite experimental evidence that it occurs[58]).

However, because of the probability that reaction 43 is thermodynamically unfavorable for the hydrido alkyl case, the reverse reaction may be thermodynamically favorable; i.e., $Os(CO)_4$ may be capable of C–H bond activation. Support for this possibility is provided by the fact that a number of the photochemically generated species recently shown to react with saturated hydrocarbons (e.g., $(C_5Me_5)Ir(PMe_3)$,[50] $(C_5Me_5)Ir(CO)$,[59] $CpIr(CO)$,[60] and $(C_5Me_5)Rh(PMe_3)$[61]) are isoelectronic[62] with, and structurally similar to, the d^8, four-coordinate, $Os(CO)_4$. The photochemical generation of $Os(CO)_4$ from $Os(CO)_5$ may thus also lead to the activation of saturated hydrocarbons.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 283 spectrophotometer calibrated with $Os_3(CO)_{12}$. Mass spectra were obtained on an AEI MS9 mass spectrometer, equipped with direct inlet and gas inlet systems, at 70 eV.

Spectroscopic Analysis of the Relative Abundance of the Various Deuterated Methanes. Methane was collected by a vacuum-line Toepler pump into a bulb which was then attached directly to the gas inlet of the mass spectrometer. All mass spectra were obtained under resolution (1:1000) sufficient to separate hydrocarbon peaks from normal background peaks (e.g., H_2O^+, OH^+, Ar^{2+}) in the region of interest (*m/e* 12–20); background scans were recorded before each gas sample was admitted to the instrument. Mass spectra of commercial methane-d_4 verified that no isotopic exchange occurred in the instrument. When only the CD_4/CD_3H ratio of the gas samples was needed, it was determined directly from the intensity ratio between *m/e* 20 and *m/e* 19. When more detailed information (CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4) was needed, it was obtained by solving simultaneous equations for the intensities at *m/e* 12 through *m/e* 20 in terms of the known fragmentation patterns of isotopically substituted methanes.[63] Values of CD_4/CD_3H obtained in this manner agreed with those obtained directly from *m/e* 20/19 intensity ratios.

Materials. All mononuclear osmium complexes were prepared by methods previously reported[5] and handled on a high-vacuum line; the standard reaction vessel was a 25-mL glass bulb connected through a high-vacuum Teflon stopcock to an O-ring joint. Deuterium-labeled derivatives ($Os(CO)_4(H)CD_3$, $Os(CO)_4(D)CH_3$, $Os(CO)_4(H)C_2D_5$, $Os(CO)_4(D)C_2H_5$, $Os(CO)_4(CD_3)_2$, $Os(CO)_4(C_2D_5)_2$) were prepared by the substitution, in the previously reported preparation, of the appropriate deuterated reagent (CD_3OSO_2F and CF_3CO_2D were commercially available; CD_3OTs was prepared from an established procedure;[64] C_2D_5OTs and $C_2D_5OSO_2F$ were prepared as described below.) Isotopic purity was established by ^1H NMR; when below 95%, as it was (despite D_2O pretreatment of the vacuum line section used) for the $Os(CO)_4(D)R$ complexes prepared by protonation with CF_3CO_2D, appropriate corrections for the actual amount of $Os(CO)_4(D)R$ present were applied to the results of crossover experiments. $(^{13}CH_3)_2Os(CO)_4$ was prepared from $Na_2Os(CO)_4$ and $^{13}CH_3I$.

Ethyl-d_5 *p*-toluenesulfonate was prepared by a slight modification of the procedure of House and Pitt[64] for the synthesis of its methyl analogue. A solution of ethanol-d_6 (2.00 g, 38.5 mmol) and *p*-toluenesulfonyl chloride (10.65 g, 55.9 mmol) in 100 mL of freshly distilled anhydrous γ-collidine was stirred at room temperature for 12 h. An additional 1.00 g (19.3 mmol) of ethanol-d_6 was then added to the collidine solution and the mixture stirred for an additional 3 h. After workup by the usual procedure,[64] the fraction distilling at 150–160 °C (10 torr) was redistilled to give ethyl-d_5 *p*-toluenesulfonate (1.57 g, 7.7 mmol, 14% yield), bp 158–162 °C (10 torr). The product showed >95% deuterium incorporation by NMR analysis.

Ethyl-d_5 fluorosulfate was prepared by a procedure analogous to that reported for the undeuterated compound.[7] C_2D_5OD (3.0 g, 58 mmol) was placed in a 10-mL round-bottomed flask cooled in ice water, and 4.0 mL of chlorosulfuric acid (HSO_3Cl) (61 mmol) was added slowly dropwise. When the addition of acid was complete, the reaction was allowed to stir for 30 minutes. Vacuum distillation at 50 °C produced $(C_2D_5)_2SO_4$ as a colorless liquid (2 mL, 49% yield).

$(C_2D_5)_2SO_4$ (0.60 mL, 4.3 mmol) was placed in a nitrogen-filled standard 25-mL vacuum line bulb containing a small magnetic stir bar. To this was added fluorosulfuric acid (FSO_3H) (0.21 mL, 3.6 mmol). This mixture was then sealed and allowed to stir at room temperature for 60 h. The vial was then opened to high vacuum at room temperature, and the product was distilled into a −195 °C cold trap. Drying over P_2O_5 gave 156 mg of $C_2D_5SO_3F$ (34% yield). An NMR spectrum of this material showed >95% deuterium incorporation.

Thermolysis of a Mixture of *cis*-$Os(CO)_4(H)CD_3$ and *cis*-$Os(CO)_4(D)CH_3$. $Os(CO)_4(H)CD_3$ (25.3 mg, 0.079 mmol) and $Os(CO)_4(D)CH_3$ (22.9 mg, 0.072 mmol, 48% D) were vacuum transferred into a standard reaction bulb with methylcyclohexane (15 mL). After the mixture was heated to 49 °C for 7.5 h, the −196 °C volatiles were collected by Toepler pump. Mass spectroscopic analysis of these volatiles showed the presence of CD_4, CD_3H, CH_3D, and CH_4. The CD_3H/CD_4 ratio, 2.7, implied that k_H/k_D was 1.2. A series of similar experiments gave an average k_H/k_D value of 1.1.

Thermolysis of a Mixture of *cis*-$Os(CO)_4(H)C_2D_5$ and *cis*-$Os(CO)_4(D)C_2H_5$. $Os(CO)_4(H)C_2D_5$ (21 mg, 0.062 mmol) and $Os(CO)_4(D)C_2H_5$ (18.7 mg, 0.056 mmol, 40% D) were vacuum transferred into a standard reaction bulb with *n*-octane (3 mL) and degassed. After 15 h at 35 °C the material that was volatile at −78 °C (just over 0.5 equiv) was collected by Toepler pump. Mass spectroscopic analysis of these volatiles showed the presence of C_2D_6, C_2D_5H, and other deuterated ethanes (their presence and concentrations were difficult to quantify because of fragmentation peaks due to C_2D_6 and C_2D_5H).

Thermolysis of *cis*-$Os(CO)_4(H)CH_3$ under CD_4. *cis*-$Os(CO)_4(H)CH_3$ (46 mg) was placed under CD_4 (0.08 atm, 1 equiv) in a standard reaction bulb. The mixture was held at 25 °C for 72 h, at which time all −196 °C volatiles were collected by Toepler pump and analyzed by mass spectrometry. Only CH_4 and CD_4 were detected.

Kinetics of the Thermolysis of *cis*-$Os(CO)_4(H)R$. The rate of disappearance of *cis*-$Os(CO)_4(H)R$ was measured in methylcyclohexane solution by monitoring the disappearance of the IR absorption at 2063 cm^{-1} (R = CH_3) or 2060 (R = C_2H_5) cm^{-1}. Product absorption at this frequency was slight and was confined to the primary product, $HOs_2(CO)_8R$.

A solution of $Os(CO)_4(H)R$, generally 0.01 M, was frozen and degassed in a standard reaction bulb. The bulb was placed in a constant temperature bath (± 0.2 °C) and was removed at appropriate intervals and cooled with ice water in order to stop

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[58] Pearson, R. G.; Mauermann, H. *J. Am. Chem. Soc.* **1982**, *104*, 500.

[59] Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723.

[60] Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190.

[61] Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562.

[62] The fact that d^8 CpML species and $Fe(CO)_4$ are isoelectronic has recently been emphasized by: Hofmann, P.; Padmanabhan, M. *Organometallics* **1983**, *2*, 1273.

[63] American Petroleum Institute Mass Spectroscopic Tables, Series Numbers 455–458.

[64] House, H. O.; Pitt, C. G. *J. Org. Chem.* **1966**, *31*, 1062.

the reaction. Aliquots were then removed under argon and their IR spectra recorded.

Scan speeds were slow enough to ensure spectrophotometric accuracy but not slow enough for noticeable reaction to occur in the IR cell during the scan. Repeat scans gave absorbance values identical with the first ones within experimental error (±0.005 absorbance units). Reactions were generally followed for at least 2 half-lives, and satisfactory linear plots were obtained throughout. Uncertainties given are the least-squares standard deviations, and the correlation coefficient, a measure of the degree of linearity, was at least 0.998 in all cases.

Kinetics of the Thermolysis of *cis*-$Os(CO)_4(H)CH_3$ in the Presence of Excess Nucleophiles. The rate of decomposition of $Os(CO)_4(H)CH_3$ in the presence of excess nucleophiles was measured by monitoring the disappearance of the infrared absorption at 2028 cm^{-1}. In a typical experiment 9.5 mg of $Os(CO)_4(H)CH_3$ was dissolved in 3 mL of methylcyclohexane along with 6.24 mg of $P(C_2H_5)_3$ (alternatively, 164.6 mg of $P(C_6H_5)_3$, 206.3 mg of $P(OCH_3)_3$, or 234.7 mg of pyridine was used). The procedures used were the same as those described above for the kinetics of the thermolysis of $Os(CO)_4(H)CH_3$ with no added nucleophile, with the exception that the absorbance/time data were treated according to eq 20.

Thermolysis of *cis*-$Os(CO)_4(H)CD_3$ and *cis*-$Os(CO)_4(D)CH_3$ in the Presence of Triethylphosphine. $Os(CO)_4(H)CD_3$ (26.3 mg) and $Os(CO)_4(D)CH_3$ (23.2 mg) were vacuum transferred with triethylphosphine (2 g) into a bulb containing methylcyclohexane (15 mL). The solution was then heated to 46 °C for 15 h, at which time all −196 °C volatiles were collected by Toepler pump. Mass spectroscopic analysis showed the absence of CD_4.

Thermolysis of *cis*-$Os(CO)_4(H)CH_3$ with Triethylphosphine under ^{13}CO. *cis*-$Os(CO)_4(H)CH_3$ (14.9 mg) was vacuum transferred into a standard reaction bulb along with methylcyclohexane (3 mL) and PEt_3 (0.591 g); thawing gave a solution with no dissolved gas. ^{13}CO (90 atom %) (0.23 atm) was then added and the mixture stirred at room temperature for 42 h, or 0.9 half-life. (This slow rate of reaction insured that mass transport of the ^{13}CO could compete effectively with the isotopically normal CO arising from any dissociative process.) An aliquot was then removed and its IR spectrum recorded. The spectrum was a combination of the known spectra of $Os(CO)_4(H)CH_3$ and $Os(CO)_4(PEt_3)$, with no additional bands, or changes in band intensity, due to ^{13}CO incorporation in either product or unreacted starting material.

Thermolysis of *cis*-$Os(CO)_4(H)CH_3$ under ^{13}CO. *cis*-$Os(CO)_4(H)CH_3$ (60 mg) was vacuum transferred into methylcyclohexane (3.5 mL); additional freeze–pump–thaw cycles ensured that the resulting solution contained no dissolved gases. ^{13}CO (90 atom %) (0.1 atm, 3 equiv) was then admitted, and the system sealed. At the same time, a second mixture was prepared containing *cis*-$Os(CO)_4(H)CH_3$ (67 mg), methylcyclohexane (3.5 mL), and isotopically normal CO (0.1 atm, 3 equiv). The contents of both vials were then stirred at room temperature for 24 h, or 1 half-life. (This slow rate of reaction ensured that mass transport of the ^{13}CO could compete effectively with the isotopically normal CO arising from any dissociative process.[65,66]) An aliquot of each was removed and the carbonyl region IR recorded. The two spectra were identical, showing that external CO had not been incorporated into either unreacted starting material or the reaction products.

Kinetics of the Thermolysis of *cis*-$Os(CO)_4(H)C_2H_5$ in the Presence of Excess $(C_2H_5)_3P$. The rate of decomposition of $Os(CO)_4(H)C_2H_5$ in the presence of excess $(C_2H_5)_3P$ was measured by monitoring the disappearance of the infrared absorptions at 2042 and 2028 cm^{-1}. The rate of formation of $(C_2H_5)_3POs(CO)_4$, the product of the reaction of $Os(CO)_4(H)C_2H_5$ with $(C_2H_5)_3P$, was also measured by monitoring the appearance of the infrared absorption at 1976 cm^{-1}. The procedures used were the same as those described above for the thermolysis of $Os(CO)_4(H)R$ with no $(C_2H_5)_3P$ added. In a typical case observation at any of the three frequencies gave essentially the same rate constant (for example, 2.28×10^{-5} s^{-1} at 2042 cm^{-1}, 2.24×10^{-5} s^{-1} at 2028 cm^{-1}, and 2.29×10^{-5} s^{-1} at 1976 cm^{-1}).

Thermolysis of *cis*-$Os(CO)_4(CH_3)_2$ with Methane-d_4. A mixture of $Os(CO)_4(CH_3)_2$ (44.1 mg) and CD_4 (93 mm Hg, 1 equiv) was heated to 162.5 °C for 1 week. The gas mixture evolved (−196 °C volatiles) was analyzed by mass spectroscopy and shown to contain a peak at m/e 19 corresponding to CD_3H.

Thermolysis of a Mixture of *cis*-$Os(CO)_4(CH_3)_2$ and $Os(CO)_4(^{13}CH_3)_2$. *cis*-$Os(CO)_4(CH_3)_2$ (37.1 mg) and *cis*-$Os(CO)_4(^{13}CH_3)_2$ (27.5 mg) were thoroughly mixed by several bulb-to-bulb transfers on the vacuum line. A small portion (10 mg) of this mixture was retained for mass spectroscopic analysis. The remainder of this mixture was heated to 162.5 °C for 3 days, at which time all products volatile at −35 °C were removed. Unreacted starting material present was then isolated by vacuum transfer at room temperature and analyzed by mass spectrometry. The mass spectrum differed from that of the initial $Os(CO)_4(CH_3)_2/Os(CO)_4(^{13}CH_3)_2$ mixture and showed the presence of $Os(CO)_4(CH_3)(^{13}CH_3)$ also.

Thermolysis of *cis*-$Os(CO)_4(CD_3)_2$ in Mixtures of Deuterated and Undeuterated *n*-Dodecane. Mixtures of *n*-$C_{12}H_{26}$ and *n*-$C_{12}D_{26}$ were prepared by syringing quantities of each, under nitrogen, into a bulb. The total volume was kept at 1 mL. The bulbs were weighed after each addition to determine the proportions of each compound used. To each of these mixtures was added $Os(CO)_4(CD_3)_2$ (31 mg); the mixture was then heated to 162.5 °C for 3 days. At that time the mixtures were cooled, and the −196 °C volatiles collected by Toepler pump and analyzed by mass spectrometry.

Attempted Observation of CIDNP in the Thermolysis of *cis*-$Os(CO)_4(CH_3)_2$. An NMR tube containing $Os(CO)_4(CH_3)_2$ (47 mg) in mesitylene (0.4 mL) was sealed under vacuum, as was a second NMR tube containing $Os(CO)_4(CH_3)_2$ (44.1 mg) in dimethylphthalate (0.4 mL). The ^1H NMR spectra of these samples were then recorded at various temperatures ranging from 160 to 200 °C. No evidence of emission or enhanced absorption was noted. After 15 min at 198 °C no significant decomposition of the *cis*-$Os(CO)_4(CH_3)_2$ had occurred.

Thermolysis of a Mixture of *cis*-$Os(CO)_4(C_2D_5)_2$ and *cis*-$Os(CO)_4(C_2H_5)_2$. $Os(CO)_4(C_2D_5)_2$ (24.1 mg, 0.065 mmol) and $Os(CO)_4(C_2H_5)_2$ (24.9 mg, 0.069 mmol) were vacuum transferred into a standard reaction bulb; 3 mL of *n*-octane was then added, and the mixture was frozen and degassed. The bulb was heated at 126 °C for 72 h and then was cooled to −78 °C while all volatile material was collected in another flask by Toepler pump. One equivalent of gas was volved per equivalent of Os. The gas-containing flask was connected to an evacuated gas IR cell equipped with a side arm into which the ethylene (0.086 mmol) was condensed at −196 °C. IR analysis after evaporation showed all possible isomers of all possible deuterated ethylenes.[26]

Reaction of *cis*-$Os(CO)_4H_2$ with $Bu_4N[RhI_3(CO)(COCH_3)]$. *cis*-$Os(CO)_4H_2$ (32.9 mg) was dissolved in CH_2Cl_2 (2 mL) along with 83.8 mg of $Bu_4N[RhI_3(CO)(COCH_3)]$[45] and the mixture heated to 49 °C for 5 h. After the mixture was cooled, the −196 °C volatiles were collected by Toepler pump. Pressure–volume measurements indicated the formation of 1 equiv of gas/equiv of rhodium. Mass spectroscopic analysis of this gas identified it as methane.

When the reaction was carried out in an NMR tube, it was evident that a small quantity of acetaldehyde was also produced.

Attempted Protonolysis of $Bu_4N[RhI_3(CO)(COCH_3)]$. $Bu_4N[RhI_3(CO)(COCH_3)]$[45] (31.8 mg) was dissolved in 1 mL of acetonitrile. On the vacuum line trifluoroacetic acid (19.7 mg) was distilled into the reaction bulb. The bulb was closed, heated to 49 °C for 6 h, and then cooled. There were no products volatile at −196 °C; an NMR of the room temperature volatiles showed no acetaldehyde.

Reaction of *cis*-$Os(CO)_4H_2$ with $Ir(CO)_2Cl_2(AsPh_3)(CH_3)$. $Ir(CO)_2Cl_2(AsPh_3)(CH_3)$[46] (22.2 mg) was combined with $Os(CO)_4H_2$

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(65) Assuming that the ^{13}CO concentration in solution is at least 10^{-3} M in these experiments (the concentration of CO in *n*-heptane is 1.2×10^{-2} M at 25 °C under 1 atm of CO[66]) and extrapolating k_1^{Me} to room temperature as 8.3×10^{-6} s^{-1}, it can be seen that at least 40 min of a dissociative reaction would be required to produce a concentration of isotopically normal CO equivalent to that of the ^{13}CO initially present in solution. At any given time the concentration of ^{13}CO is therefore much larger than that of any dissociated CO.

(66) Linke, W. F.; Seidell, A. "Solubilities: Inorganic and Metal-Organic Compounds", 4th ed.; American Chemical Society: Washington, DC, 1958; Vol. I, p 456.

(83.6 mg) in 3 mL of methylcyclohexane. After the mixture was heated to 49 °C for 20 h, the products volatile at −196 °C were collected by Toepler pump (3 equiv/equiv of iridium). GLC analysis (N_2 as carrier gas, 20-ft Porapak QS column, Perkin-Elmer 3920 gas chromatograph equipped with a thermal conductivity detector and a gas switching valve connected to the vacuum line Toepler pump) revealed equimolar quantities of CH_4, CO, and H_2. IR analysis of the metal-containing products of the reaction revealed the presence of $Ir_4(CO)_{12}$.[67]

Kinetics of the Reaction of *cis*-$Os(CO)_4H_2$ with $Ir(CO)_2Cl_2(AsPh_3)(CH_3)$. $Os(CO)_4H_2$ (33.6 mg, 0.11 mmol) was combined with $Ir(CO)_2Cl_2(AsPh_3)(CH_3)$ (12.5 mg, 0.02 mmol) in chlorobenzene (3 mL). The reaction was carried out at 49 °C, and at appropriate time intervals aliquots were removed from the reaction flask and their carbonyl region IR spectra recorded. In this manner it was possible to determine the rate of disappearance of both $Os(CO)_4H_2$ and $Ir(CO)_2Cl_2(AsPh_3)(CH_3)$.

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Appendix A

Derivation of Integrated Rate Law (Eq 20) for Competition Experiments in Which One Competitor is Starting Material (Scheme I).

$$cis\text{-}Os(CO)_4(H)CH_3 \xrightarrow{k_2} X$$

$$X + Os(CO)_4(H)CH_3 \xrightarrow[\text{fast}]{k_3} CH_4 + HOs_2(CO)_8CH_3$$

$$X + L \xrightarrow[\text{fast}]{k_4} CH_4 + Os(CO)_4L$$

Let

$$s = [Os(CO)_4(H)CH_3]$$
$$x = [X]$$
$$L = [L]$$

Beginning with the disappearance of starting material

$$ds/dt = -k_2s - k_3sx \qquad (A1)$$

and substituting the steady-state value for x

$$\frac{ds}{dt} = -k_2s - \frac{k_2k_3s^2}{k_3s + k_4L} \qquad (A2)$$

$$\frac{ds}{dt} = \frac{-2k_2k_3s^2 - k_2sk_4L}{k_3s + k_4L} \qquad (A3)$$

Upon integration we obtain

$$t\ (+\ \text{constant}) = \frac{1}{2k_2}\ln(-k_2k_4L - 2k_2k_3s) - \frac{1}{k_2}\ln(s) \qquad (A4)$$

which upon evaluation between $t = 0$, $s = s_0$ and $t = t$, $s = s$ yields

$$t = \frac{1}{2k_2}\ln\frac{k_4L + 2k_3s}{k_4L + 2k_3s_0} - \frac{1}{k_2}\ln\left(\frac{s}{s_0}\right) \qquad (A5)$$

which upon rearrangement gives

$$2k_2t + 2\ln\left(\frac{s}{s_0}\right) = \ln\left(\frac{k_4L + 2k_3s}{k_4L + 2k_3s_0}\right) \qquad (A6)$$

Now we define the left-hand side of the equation as C and write

$$C = \ln\left(\frac{k_4L + 2k_3s}{k_4L + 2k_3s_0}\right) \qquad (A7)$$

In exponential form

$$e^C = \left(\frac{k_4L + 2k_3s}{k_4L + 2k_3s_0}\right) \qquad (A8)$$

which gives

$$\frac{k_4}{k_3} = \frac{2s - 2s_0e^C}{Le^C - L} \qquad (A9)$$

and

$$2s - 2s_0e^C = \frac{k_4}{k_3}(Le^C - L) \qquad (A10)$$

which is eq 20.

Appendix B

For Scheme II

$$\frac{[CD_4]}{[CD_3H]} = \frac{k_D[C_{12}D_{26}] + k_6[Os(CO)_4(CD_3)_2]_0}{k_H[C_{12}H_{26}]} \qquad (B1)$$

as $[Os(CO)_4(CD_3)_2]_0$ is effectively the concentration of $Os(CO)_4(CD_3)_2$ throughout the reaction

$$\frac{[CD_4]}{[CD_3H]} = \frac{k_D(1 - y)[S]}{k_Hy[S]} + \frac{k_6[Os(CO)_4(CD_3)_2]_0}{k_Hy[S]} \qquad (B2)$$

where [S] is the total concentration of dodecane solvent

$$\frac{[CD_4]}{[CD_3H]} = \frac{k_D}{k_H}\left(\frac{1 - y}{y}\right) + \frac{R}{y} \qquad (B3)$$

as R, the $[CD_4]/[CD_3H]$ ratio in pure $C_{12}H_{26}$, is $k_6[Os(CO)_4(CD_3)_2]_0/k_H[S]$. For Scheme III, the steady-state approximation in [Y] gives

$$[Y] = \frac{k_5[Os(CO)_4(CD_3)_2]_0}{k_H[C_{12}H_{26}] + k_D[C_{12}D_{26}]} \qquad (B4)$$

and

$$\frac{d[CD_4]}{dt} = \frac{k_Dk_5[Os(CO)_4(CD_3)_2]_0[C_{12}D_{26}]}{k_H[C_{12}H_{26}] + k_D[C_{12}D_{26}]} + k_7[Os(CO)_4(CD_3)_2]_0 \qquad (B5)$$

As

$$\frac{d[CD_3H]}{dt} = \frac{k_Hk_5[Os(CO)_4(CD_3)_2]_0[C_{12}H_{26}]}{k_H[C_{12}H_{26}] + k_D[C_{12}D_{26}]} \qquad (B6)$$

$$\frac{[CD_4]}{[CD_3H]} = \frac{k_D[C_{12}D_{26}]}{k_H[C_{12}H_{26}]} + \frac{k_Hk_7[C_{12}H_{26}] + k_Dk_7[C_{12}D_{26}]}{k_Hk_5[C_{12}H_{26}]}$$

$$\frac{[CD_4]}{[CD_3H]} = \frac{[C_{12}D_{26}]}{[C_{12}H_{26}]}\frac{k_D}{k_H}\left(1 + \frac{k_7}{k_5}\right) + \frac{k_7}{k_5} \qquad (B7)$$

As R, the CD_4/CD_3H ratio in pure $C_{12}H_{26}$, is k_7/k_5

$$\frac{[CD_4]}{[CD_3H]} = \frac{k_D}{k_H}\left(\frac{1 - y}{y}\right)(1 + R) + R \qquad (B8)$$

Registry No. *cis*-$Os(CO)_4(H)Me$, 22639-03-8; *cis*-$Os(CO)_4(H)Et$, 68568-90-1; *cis*-$Os(CO)_4(CD_3)_2$, 96617-74-2; *cis*-$Os(CO)_4$-

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(H)CD_3, 96617-84-4; *cis*-Os$(CO)_4$(D)CH_3, 96617-75-3; *cis*-Os$(CO)_4$(H)C_2D_5, 96633-19-1; *cis*-Os$(CO)_4$(D)C_2H_5, 96617-76-4; *cis*-Os$(CO)_4(CH_3)_2$, 22639-01-6; *cis*-Os$(CO)_4(^{13}CH_3)_2$, 96617-77-5; *cis*-Os$(CO)_4(C_2D_5)_2$, 96617-78-6; *cis*-Os$(CO)_4(C_2H_5)_2$, 27882-33-3; *cis*-Os$(CO)_4H_2$, 18972-42-4; $Bu_4N[RhI_3(CO)(COCH_3)]$, 96617-80-0; $Ir(CO)_2Cl_2(AsPh_3)(CH_3)$, 29860-74-0; $Ir_4(CO)_{12}$, 18827-81-1; $Na_2Os(CO)_4$, 27857-55-2; $[Os(CO)_4H]^-$, 44864-29-1; $[Os(CO)_4]^{2-}$, 95325-16-9; $[Os(CO)_4D]^-$, 96617-83-3; $Os(CO)_4(PEt_3)$, 61763-56-2; $(OC)_4HOs–OsCH_3(CO)_4$, 60442-71-9; PEt_3, 554-70-1; PPh_3, 603-35-0; $P(OCH_3)_3$, 121-45-9; *n*-$C_{12}D_{26}$, 16416-30-1; $^{13}CH_3I$, 4227-95-6; $(C_2D_5)_2SO_4$, 96617-81-1; $C_2D_5SO_3F$, 96617-82-2; CD_3OSO_2F, 83803-45-6; CD_3OTs, 7575-93-1; C_2D_5OTs, 59034-23-0; C_2D_5OH, 1516-08-1; pyridine, 110-86-1; *n*-dodecane, 112-40-3; di-*n*-pentyl ether, 693-65-2; phenetole, 103-73-1; *sec*-butylbenzene, 135-98-8; 2-octanone, 111-13-7; acetophenone, 98-86-2; 1,2,3,4-tetramethylbenzene, 488-23-3; ethyl-d_5 *p*-toluenesulfonate, 59034-23-0.

Mechanistic Study of the Reactions of 1,1-Dimethylallene with Nickel(0) Complexes. π- and σ-Complex Formation vs. Electron Transfer

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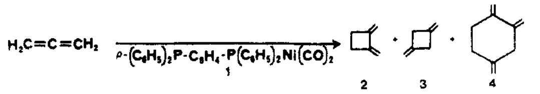
The reactions of 1,1-dimethylallene (DMA) with several Ni(0) complexes have been studied. Kinetic and NMR studies on the reaction of DMA with tris(triphenylphosphine)nickel(0) $[(TPP)_3Ni]$ indicate the formation of mono(1,1-dimethylallene)-, *cis*- and *trans*-bis(1,1-dimethylallene)-, and tris(1,1-dimethylallene)nickel complexes, the ratio of the complexes depending on the concentration of DMA and added TPP. At temperatures below −60 °C the *cis*-bis(DMA) π-complex [and possibly the tris(DMA) π-complex] undergoes coupling to form mainly the 3,4-bis(isopropylidene)nickelacyclopentane complex **30**. At temperatures above −15 °C, **30** undergoes hydrogen atom migration and reductive elimination to form **12**. The reaction of tris(triethylphosphine)nickel(0) with DMA also results in the formation of **12**; however, the extent of mono-, bis-, and tris(DMA) π-complex formation is much less. In contrast, DMA reacts with $(COD)_2Ni$ in an electron-transfer process to initially form the DMA radical anion. The overall reaction is very complex. Carbonylation of the finally derived complex(es) produces the two isomeric, trimeric ketones **22** and **24**. The reaction of DMA with the mixed-ligand complexes (cyclooctadiene)(triphenylphosphine)nickel(0) and (cyclooctadiene)(ethyl acrylate)nickel(0) proceed in a manner similar to that with the substituted-phosphine complexes.

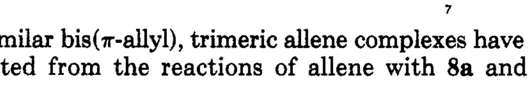
Introduction

The reactions of substituted alkenes, dienes, and alkynes with Ni(0) complexes result in coupling, cyclic and linear oligomerization, and polymerization and have been extensively studied.[1] In contrast, the reactions of substituted allenes with Ni(0) complexes have received considerably less attention, most of the attention having been focused on the reactions with allene itself.

The earliest report appears to be that by Otsuka and co-workers[2] who reported that the reaction of an excess of allene with several Ni(0) and Ni(I) complexes resulted in the regular, linear polymerization to produce crystalline 1,2-polyallene. Later investigations were devoted to a study of the mechanism of polymerization and the structures of intermediates initially formed during the polymerization process.

The reaction of allene in the gas phase at 175–225 °C over a solid-phase catalyst having the composition 1 resulted in the formation of a mixture of the two bis(methylene)cyclobutanes 2 and 3, and a mixture of trimers consisting mostly of 4.[3] The solution-phase reactions of allene in the presence of 1, $(COD)_2Ni^0$,[4] or bis(triphenylphosphine)nickel(0) $[(TPP)_2Ni]$[5] result in the formation of mixtures of cyclic tetramers, pentamers, and higher molecular weight oligomers. De Pasquale[5] claimed to have isolated and characterized a complex having structure **5** (mp 60–61 °C) which in solution dissociates to **6**. However, in a later low-temperature NMR study of the reaction of allene with $(TPP)_2Ni(C_2H_4)$ in a 1:1 ratio, Otsuka and co-workers[6] characterized a monoallene π-complex which at temperatures *above* −10 °C reacted to produce a trimeric allene complex whose structure was shown to be **7** by X-ray diffraction. Further reaction of **7** with additional allene produced a tetrameric allene, bis(π-allyl) complex.[6]





Similar bis(π-allyl), trimeric allene complexes have been isolated from the reactions of allene with **8a** and **8b**.[7]

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