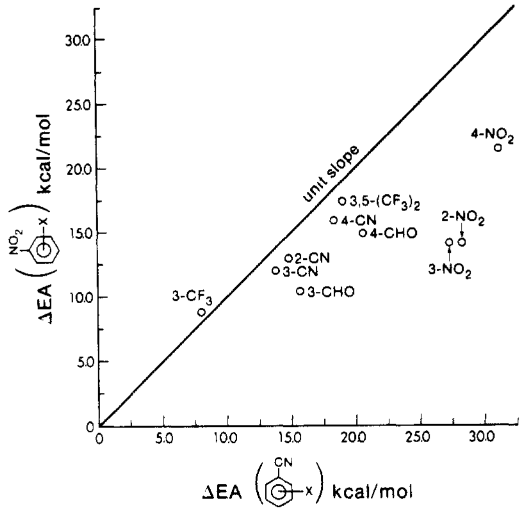

Figure 11. Relative electron affinities. Substituted cyanobenzenes vs. substituted nitrobenzenes.

with decreasing SOMO ring density than the field effect.

A comparison between the effect of a larger variety of substituents X in positions 2, 3, and 4 on the electron affinities of cyanobenzene and nitrobenzene is given in Figure 11. The substituents which have a strong field effect and small resonance effect (CF_3, 3,5-$(CF_3)_2$, 2-CN, 3-CN, 4-CN) fall close to the unit slope line, i.e., for these substituents the reduced SOMO density of the nitrobenzene ring, relative to the cyanobenzene ring, is of no great consequence. The strongly π withdrawing substituents CHO and NO_2, on the other hand, are displaced to the right, i.e., for the NO_2–C_6H_4–X these substituents produce a smaller electron affinity increase relative to the CN–C_6H_4X. These trends are in agreement with Figure 10 and attendant discussion. Interestingly, a significant displacement is observed also for the CHO and particularly NO_2 in position 3. A plot like that in Figure 11 is somewhat misleading. For example, considering the NO_2 substituent effect on $C_6H_5CN^-$, it is obvious that the NO_2 introduction leads to a large shift of SOMO density to NO_2 which is the more powerful substituent. This will happen also when NO_2 is introduced in position 3. On the other hand, when NO_2 is introduced in position 3 of $C_5H_5NO_2^-$, the SOMO density shift to it will be considerably smaller since that substituent does not overpower the equally strong initial NO_2. In other words a large decrease between the electron affinities of 4-dinitrobenzene and 3-dinitrobenzene is expected while for the pair 4-nitrocyanobenzene and 3-nitrocyanobenzene the decrease should be small, and these expected changes are observed in Figure 11.

Acknowledgment. This work was supported by the Canadian Natural Science and Engineering Research Council.

Registry No. 2,3-$(CH_3)_2$NB, 83-41-0; 4-CF_3BN, 455-18-5; 3-FNB, 402-67-5; F_4BQ, 527-21-9; 4-CNNB, 619-72-7; 3-CNNB, 619-24-9; 2-CNNB, 612-24-8; 4-CH_3NB, 99-99-0; 2-NO_2NB, 528-29-0; NB, 98-95-3; 2-CH_3NB, 88-72-2; tetracyanoethylene, 670-54-2; *trans*-1,2-dicyanoethylene, 764-42-1; 4-formylbenzonitrile, 105-07-7; 4-acetylbenzonitrile, 1443-80-7; 4-cyanobenzonitrile, 623-26-7; 3,5-dimethylbenzonitrile, 22445-42-7; 2-cyanobenzonitrile, 91-15-6; 3-formylbenzonitrile, 24964-64-5; 3-cyanobenzonitrile, 626-17-5; 4-methylbenzonitrile, 104-85-8; 2,6-dichlorobenzonitrile, 1194-65-6; 2-methylbenzonitrile, 529-19-1; 1-naphthonitrile, 86-53-3; 3-(trifluoromethyl)benzonitrile, 368-77-4; 2-naphthonitrile, 613-46-7.

Kinetics of Reaction of Dodecacarbonyltriosmium with Diphenylacetylene

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Abstract: The kinetics of reaction of $Os_3(CO)_{12}$ with C_2Ph_2 in decalin or tetradecane between 160 and 195 °C, and under various partial pressures of CO, have been studied. Loss of $Os_3(CO)_{12}$ occurs by two main paths. One involves a very unusual bimolecular reaction between C_2Ph_2 and the cluster ($k = 5.4 \times 10^{-4}$ M^{-1} s^{-1} at 170 °C; $\Delta H^* = 37.3 \pm 5.0$ kcal mol^{-1}; $\Delta S^* = 9.7 \pm 11.5$ cal K^{-1} mol^{-1}). The other involves a labile preequilibrium between $Os_3(CO)_{12}$ and $Os_3(CO)_{11}(\eta^2\text{-}C_2Ph_2)$ ($K = 2.5 \times 10^{-3}$ at 170 °C; $\Delta H° = 9.4 \pm 2.9$ kcal mol^{-1}; $\Delta S° = 9.2 \pm 6.7$ cal K^{-1} mol^{-1}) followed by slow dissociative loss of CO ($k = 4.5 \times 10^{-4}$ s^{-1} at 170.0 °C; $\Delta H^* = 32.4 \pm 1.8$ kcal mol^{-1}; $\Delta S^* = -1.6 \pm 4.3$ cal K^{-1} mol^{-1}). It is proposed that this dissociative loss of CO is accompanied by a concerted change of the $\eta^2\text{-}C_2Ph_2$ to $\mu\text{-}C_2Ph_2$ with formation of $Os_3(CO)_{10}(\mu\text{-}C_2Ph_2)$. $Os_3(CO)_{10}(\mu\text{-}C_2Ph_2)$ reacts readily with C_2Ph_2 between 80 and 95 °C in decalin to give $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ by a simple CO dissociative mechanism ($k = 6.2 \times 10^{-4}$ s^{-1} at 85 °C; $\Delta H^* = 28.0 \pm 1.8$ kcal mol^{-1}; $\Delta S^* = 4.6 \pm 5.1$ cal K^{-1} mol^{-1}). $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ fragments to form $Os_2(CO)_6(C_4Ph_4)$ and $Os(CO)_5$ between 50 and 70 °C at rates proportional to [CO] ($k = 0.41$ M^{-1} s^{-1} at 50 °C; $\Delta H^* = 8.2 \pm 1.3$ kcal mol^{-1}; $\Delta S^* = -35.3 \pm 3.9$ cal K^{-1} mol^{-1}). The bimolecular reaction of C_2Ph_2 with $Os_3(CO)_{12}$ almost certainly leads directly to fragmentation products.

Much attention has been paid in recent years to reactions of unsaturated organic molecules with metal carbonyl clusters.[1] This has been motivated by an interest in the wide variety of bonding modes possible between such molecules and small clusters of metal atoms[1,2] and by a desire to explore the possible uses of cluster compounds as homogeneous or supported catalysts.[2,3] Knowledge of the mechanisms of these reactions[4] has not accumulated as rapidly as that of the structural nature of the products, and kinetic

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(1) E.g.: *Organomet. Chem.* **1972**, *1*, et seq.

(2) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451–470; *J. Organomet. Chem.* **1980**, *200*, 177–190; *Q. Rev. Chem. Soc.* **1982**, *11*, 283–320. (b) Lewis, J.; Johnson, B. F. G. *Gazz. Chim. Ital.* **1979**, *109*, 271–289. (c) *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chichester, 1980.

(3) (a) Whyman, R. Chapter 8 in ref 2c. (b) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109–148.

(4) *Inorg. React. Mech.* **1971–1981**, *1–7*. *Inorganic and Organometallic Reaction Mechanisms*; Twigg, M. V., Ed.; Plenum: New York, 1983, Vol. 1; 1984, Vol 2; 1985, Vol. 3.

(5) Tachikawa, M. T.; Shapley, J. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 7172–7174.

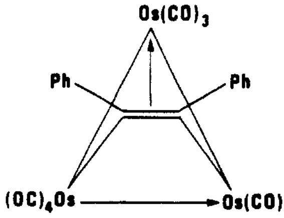
(6) Ferraris, G.; Gervasio, G. *J. Chem. Soc., Dalton Trans.* **1974**, 1813–1817.

Table I. C–O Stretching Frequencies of Some Relevant Complexes in Decalin

$Os_3(CO)_{11}(C_2H_4)$[a]	2117 (w)	2064 (s)	2048 (s)	2027 (vs)	2010 (m)	2004 (s)	1995 (m)	1984 (w)	1969 (w)
$Os_3(CO)_{11}(C_2Ph_2)$	2113 (w)	2074 (s)	2063 (s)	2044 (m)	2034 (vs)	2020 (m)	1999 (s)	1984 (m)	1967 (w)
$Os_3(CO)_{10}(C_2Ph_2)$[b]	2100 (w)	2066 (vs)	2046 (s)	2028 (s)	2009 (s)	1996 (m)	1985 (w)		
$Os_3(CO)_9(C_4Ph_4)$[c]	2113 (m)	2057 (vs)	2042 (s)	2011 (s)	1998 (m)	1988 (w)	1973 (w)	1929 (m)	
$Os_3(CO)_8(C_4Ph_4)$[c]	2094 (m)	2057 (s)	2033 (vs)	2018 (m)	2012 (m)	1998 (7)	1973 (m)		
$Os_2(CO)_6(C_4Ph_4)$[c]	2081 (s)	2051 (vs)	2015 (m)	1998 (s)	1972 (m)				

[a] Reference 9. [b] Reference 5. [c] Reference 7.

studies that are essential in acquiring such knowledge are rare. Apart from mechanistic knowledge itself, quantification of reaction rates under a wide variety of conditions is basic to developing the precise understanding of reactivity necessary for rational catalyst design. We have undertaken kinetic studies of a few such reactions and report here on a sequence beginning with the reaction of diphenylacetylene with $Os_3(CO)_{12}$ and proceeding through the known complexes $Os_3(CO)_{10}(\mu\text{-}C_2Ph_2)$, I,[4] and $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$, II,[5,6] to $Os_2(CO)_6(\mu\text{-}C_4Ph_4)$, III.[7,8]



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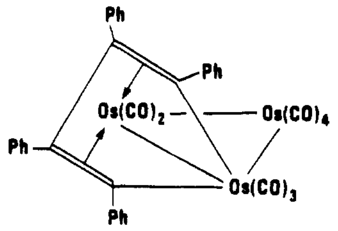

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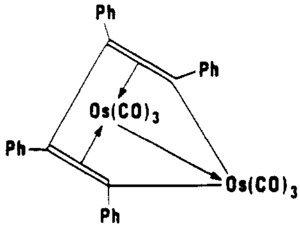


III

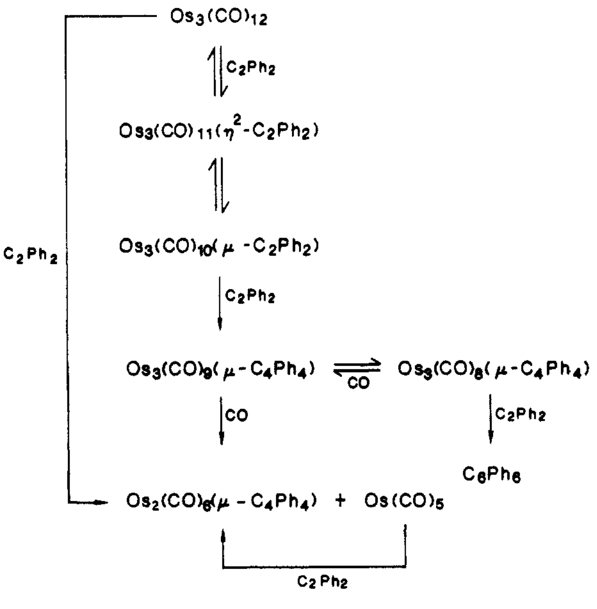
Experimental Section

$Os_3(CO)_{12}$ (Strem Chemicals) and C_2Ph_2 (Aldrich) were used as received. Decalin and tetradecane (Aldrich) were washed successively with 4 M H_2SO_4 and water, dried over $MgSO_4$, and distilled several times under reduced pressure to ensure the absence of any unsaturated impurities. They were stored over molecular sieves (Linde Type 4A). CO, N_2, and CO–N_2 mixtures of known composition were obtained from Matheson Canada Ltd. or Canox Ltd.

$Os_3(CO)_{10}(NCMe)_2$ was prepared by reaction of 2 equiv of freshly sublimed Me_3NO with $Os_3(CO)_{12}$ in dry acetonitrile at 60 °C under N_2 for a few minutes. Solvent was removed under vacuum, and small amounts of impurities were removed by washing the solid products with cold MeCN until they were spectroscopically pure.[9] $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{11}(C_2H_4)$ were prepared by the method of Johnson et al.[9]

The new complex $Os_3(CO)_{11}(C_2Ph_2)$ was prepared by reacting 1 equiv of C_2Ph_2 with $Os_3(CO)_{11}(C_2H_4)$ in dry cyclohexane at ca. 40 °C for a few minutes, the C_2H_4 being removed by bubbling with Ar. Removal of solvent gave a solid product with an IR spectrum very close to that of $Os_3(CO)_{11}(C_2H_4)$[9] (Table I). The mass spectrum showed fragments corresponding to $(M - CO)^+$ and $(M - C_2Ph_2)^+$, although no parent ion was observed. Brief exposure to CO in solution regenerates pure $Os_3(CO)_{12}$, and in the absence of CO, the complex converts very slowly to the known $Os_3(CO)_{10}(C_2Ph_2)$. All attempts to grow crystals suitable for X-ray analysis were unsuccessful. Elemental analysis always resulted in rather high results for C even when there was no evidence for any unreacted C_2Ph_2 or unremoved solvent. However, the mass spectroscopic and IR data, the reactions of the complex, and the reactions by which it was formed leave little doubt of its formulation as $Os_3(CO)_{11}(C_2Ph_2)$.

Scheme I



$Os_3(CO)_{10}(C_2Ph_2)$ was prepared in situ by reaction of $Os_3(CO)_{10}(NCMe)_2$ in decalin with a known excess of C_2Ph_2 at room temperature.[10] The reaction was complete in ca. 1.5 h as evidenced by the IR spectrum (Table I) which is in excellent agreement with published values.

$Os_3(CO)_9(C_4Ph_4)$ was prepared, also in situ, by further reaction of $Os_3(CO)_{10}(C_2Ph_2)$ with C_2Ph_2[5] for 12 h at 55 °C. This produced approximately equal amounts of $Os_3(CO)_9(C_4Ph_4)$ and $Os_3(CO)_8(C_4Ph_4)$[7] (Table I). The solutions were then cooled to room temperature and treated with CO for about 10 min when all the $Os_3(CO)_8(C_4Ph_4)$ reacted to form $Os_3(CO)_9(C_4Ph_4)$.

Kinetic Procedures. Kinetic runs were carried out on solutions prepared in Schlenk tubes fitted with rubber septum caps, shielded from room light, and thermostated to ±0.2 °C by immersion in an oil bath (Lauda Model NS-20). All solutions were purged with a stream of N_2 and then saturated, if required, with CO or CO–N_2 mixtures of known composition. Samples were withdrawn periodically by syringe under a slight pressure of gas, and the reaction was quenched by cooling to room temperature. IR spectra of the samples were recorded on a Perkin-Elmer 180 or 337 spectrophotometer. Initial concentrations of reacting complex were generally ca. 2.5–5 × 10^{-4} M.

Reactions were followed by monitoring changes in the IR spectra of bands distinct from those of any products. Values of A_∞ were therefore small and plots of ln $(A_t - A_\infty)$ vs. time were linear for at least two half-lives.

Concentrations of CO in decalin were estimated by extrapolation of the solubilities measured[11] between 20 and 75 °C. Values under 1 atm of CO were obtained by extrapolation of plots of ln $[CO]_{1\,atm}$ vs. $1/T$, and the vapor pressures of decalin were estimated, when necessary, by extrapolation of values published[12] for temperatures up to 160 °C. The values of [CO] under a 1-atm pressure of mixtures of CO, N_2, and decalin vapor could then be estimated by assuming Henry's law to hold.

Results and Discussion

The kinetic results obtained for reactions of $Os_3(CO)_{12}$, $Os_3(CO)_{10}(\mu\text{-}C_2Ph_2)$, and $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ can all be understood in terms of Scheme I.

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(7) Gambino, O.; Vaglio, G. A.; Ferrari, R. P.; Cetini, G. *J. Organomet. Chem.* **1971**, *30*, 381–386.

(8) Dodge, R. P.; Mills, O. S.; Shoemaker, V. *Proc. Chem. Soc.* **1963**, 380–381.

(9) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407–412.

(10) Tachikawa, M. T.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *124*, C19–22.

(11) Basato, M.; Fawcett, J. P.; Poë, A. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1350–1356.

(12) *Handbook of Chemistry and Physics*; Weast, R. C., Ed.; The Chemical Rubber Co.: Cleveland, OH, 1975.

Table II. Derived Rate Parameters[a] for Reaction of $Os_3(CO)_{12}$ with C_2Ph_2 in Decalin

T, °C	no. of measurements	a, s	$10^{-3}b$, s	$10^6 k_{A1}$, s^{-1}	$10^4 k_{A2}$, M^{-1} s^{-1}	$\sigma(k_{obsd})$,[b] %
160.0	8	5510 ± 163	2976 ± 147	5.77 ± 0.67	1.86 ± 0.08	4.4
165.0	8	3191 ± 73	1414 ± 83	9.95 ± 2.27	2.66 ± 0.26	8.8
170.0	22	2174 ± 46	863 ± 46	6.98 ± 1.06	5.54 ± 0.26	8.5
175.0	7	1454 ± 32	612 ± 58	8.87 ± 0.45	7.13 ± 0.06	9.4
		$\Delta H_{A2}^{\ddagger}$ = 37.3 ± 5.0 kcal mol^{-1}		$\Delta S_{A2}^{\ddagger}$ = 9.7 ± 11.5 cal K^{-1} mol^{-1}		

[a] a, b, k_{A1}, and k_{A2} are defined in eq 1 and 2. [b] Probable error (standard deviation) of an individual value of k_{obsd} (see text).

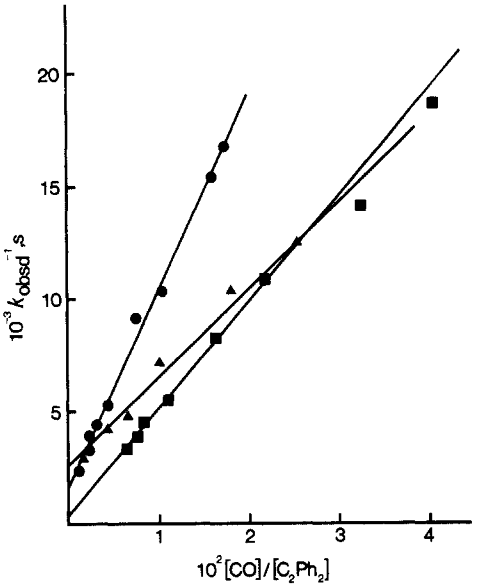

Figure 1. Dependence of $1/k_{obsd}$ on [CO]/[C_2Ph_2] for reaction of $Os_3(CO)_{12}$ with C_2Ph_2 at 170 °C. (●) 10^3[CO] = 0.081 M, [C_2Ph_2] = 0.0047–0.081 M; (■) 10^3[CO] = 1.62 M, [C_2Ph_2] = 0.04–0.25 M; (▲) 10^3[CO] = 0.081–1.62 M, [C_2Ph_2] = 0.064 M.

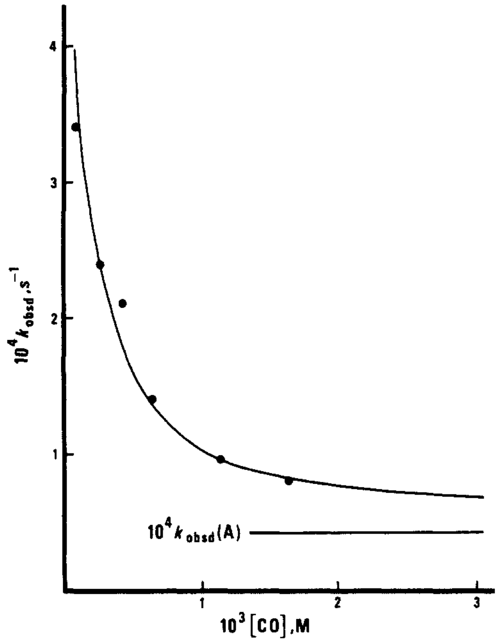

Figure 2. Dependence of k_{obsd} on [CO] for reaction of $Os_3(CO)_{12}$ with C_2Ph_2 at 170 °C in decalin. [C_2Ph_2] = 0.064 M. The horizontal line defines the value of k_{obsd} for reaction with 0.064 M C_2Ph_2 in tetradecane and [CO] = ca. 6 × 10^{-3} M.

Reactions of $Os_3(CO)_{12}$. Reactions of $Os_3(CO)_{12}$ with C_2Ph_2, in decalin at 160–175 °C, proceed under Ar to form $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$,[6] $Os_3(CO)_8(\mu\text{-}C_4Ph_4)$,[13] and hexaphenylbenzene.[14] Rates were strongly affected by CO and reactions were monitored by following the decreasing intensity of the band at 2066 cm^{-1}, due to $Os_3(CO)_{12}$, under known partial pressures of CO. Under these conditions $Os_3(CO)_8(\mu\text{-}C_4Ph_4)$ is not formed and $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ reacts to form $Os_2(CO)_6(\mu\text{-}C_4Ph_4)$. Decreasing amounts of C_6Ph_6 are formed as [CO] is increased.

The values of k_{obsd} for reaction under 5% CO at 170 °C increase with [C_2Ph_2] but appear to approach a limiting value. An excellent linear plot of $1/k_{obsd}$ against [CO]/[C_2Ph_2] is obtained (Figure 1) as expected for a simple dissociative reaction. However, although a good linear plot of $1/k_{obsd}$ against [CO]/[C_2Ph_2] is also obtained for reactions under 100% CO, the line does not coincide with that from data under 5% CO as should be the case for the simple dissociative mechanism. Further, a *third* straight line is obtained (Figure 1) for data when reactions were carried out under various partial pressures of CO with constant [C_2Ph_2]. A clue to the resolution of this complex behavior is provided in Figure 2 which shows that k_{obsd} appears to decrease with [CO] toward a lower limiting value, independent of [CO]. This is supported by the observation of quite substantial residual reaction under 100% CO in tetradecane. Tetradecane has a much lower vapor pressure[12] at 170 °C than decalin, and the solubility of CO is consequently higher. An additional factor is the generally greater solubility of CO in straight-chain aliphatic solvents,[11,15] and we estimate [CO] to be ca. 6 × 10^{-3} M in tetradecane at 170 °C as compared to 1.6 × 10^{-3} M in decalin. The rate constant under CO in tetradecane at 170 °C, shown by the horizontal line in Figure 2, corresponds to a reasonable lower limit for the k_{obsd} vs. [CO] data. At 190 °C the rate constants for reaction in tetradecane increase linearly with [C_2Ph_2], and these results all suggest that there is a [CO]-independent, but [C_2Ph_2]-dependent, path (path A) as well as another (path B) that follows kinetics characteristic of a CO dissociative mechanism.

The contribution of path A to reaction in decalin can be estimated quite precisely on the basis of the rate equations shown in eq 1a and 1b, eq 1b corresponding to the CO dissociative mechanism. The contribution of path A to the overall rate is

$$k_{obsd} = k_A + k_B \qquad (1a)$$

$$1/k_B = a + b[CO]/[C_2Ph_2] \qquad (1b)$$

obviously smallest for reactions under 5% CO, and we can take k_{obsd}(5%) as an approximate measure of k_B. Preliminary values of a and b found from the intercept and gradient of the linear plot of $1/k_{obsd}$(5%) against [CO]/[C_2Ph_2] in Figure 1 can then be used to estmate values of k_B(100%) for the various values of [CO]/[C_2Ph_2] used for reactions under 100% CO. These are all substantially less than the corresponding values of k_{obsd}(100%) and the difference provides initial values of k_A. These are found to depend on [C_2Ph_2] (eq 2 and Figure 3) in the same way as the values of k_{obsd} for reaction in tetradecane under CO at 190 °C.

$$k_A = k_{A1} + k_{A2}[C_2Ph_2] \qquad (2)$$

The initial estimates of k_{A1} and k_{A2} are then used to provide better estimates of k_B(5%) from k_{obsd}(5%) and thence better estimates of a and b. These can be used to provide new values of k_B(100%), k_{A1}, and k_{A2}. This iteration was continued until the values of a, b, k_{A1}, and k_{A2} became constant. The final values of these parameters and their standard deviations[16] are given in Table II

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(13) Ferraris, G.; Gervasio, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1057–1061.

(14) Characterized by its IR spectrum and melting point.

(15) Bor, G.; Dietler, U. K.; Pino, P.; Poë, A. J. *J. Organomet. Chem.* **1978**, *154*, 301–315. Note especially the footnote on p 308.

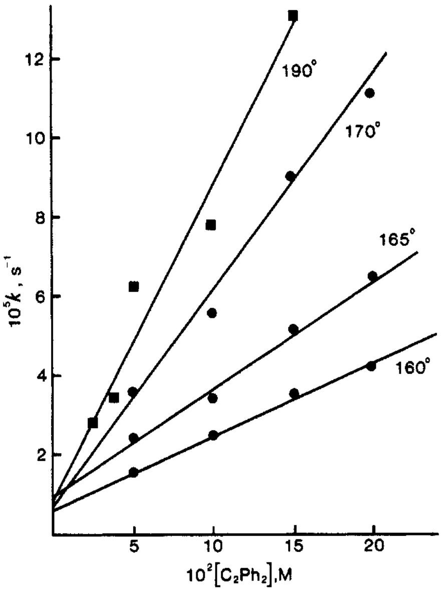

Figure 3. Dependence of k on $[C_2Ph_2]$ for reaction of $Os_3(CO)_{12}$ with C_2Ph_2. (●) $k = k_A = k_{obsd} - k_B$ for reaction in decalin. (■) $k = 0.2k_{obsd}$ for reaction in tetradecane under CO.

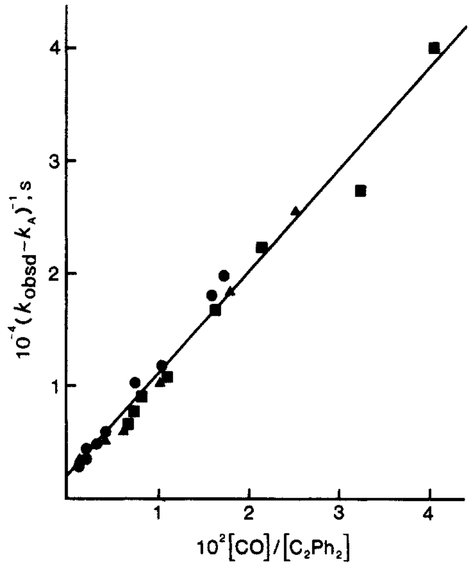

Figure 4. Dependence of $1/(k_{obsd} - k_A)$ on $[CO]/[C_2Ph_2]$ for reaction of $Os_3(CO)_{12}$ with C_2Ph_2 at 170 °C. The different data points are as defined for Figure 1.

together with those obtained in an identical way from data at other temperatures. Values of $1/k_B$ at 170 °C, estimated from $k_{obsd} - k_A = k_B$, are plotted against $[CO]/[C_2Ph_2]$ in Figure 4, showing that the complexity of Figure 1 has been completely resolved. The parameters in Table II enable expected values, k_{calcd}, to be estimated for the various values of $[CO]/[C_2Ph_2]$ at a given temperature, and from these, we calculate $\sigma(k_{obsd}) = 100\{\sum\Delta^2/(N - 4)\}^{1/2}$, where $\Delta = (k_{obsd} - k_{calcd})/k_{calcd}$. Values of $\sigma(k_{obsd})$ are given in Table II and show that the data are in excellent quantitative agreement with rate equations (1a), (1b), and (2) over a very wide range of conditions.

Although eq 1b is characteristic of a simple CO dissociative mechanism, with CO and C_2Ph_2 competing for $Os_3(CO)_{11}$, this cannot be the mechanism. The rate constant for substitution of PPh_3 into $Os_3(CO)_{12}$ at 160 °C is 108 × 10^{-4} s^{-1},[18] irrespective of $[PPh_3]$. This can be concluded[17] to be the rate constant for CO dissociation and is much greater than the values $1/a$ = 1.9 × 10^{-4} s^{-1} (Table II). Reaction of $Os_3(CO)_{11}(C_2Ph_2)$ with CO was also shown to be very fast, and eq 1b is therefore in much better accord with the mechanisms shown in eq 3 and 4,[20] reaction 3 being a labile equilibrium. The corresponding rate equation is shown in eq 5 so that $1/a = k_4$ and $1/b = K_3k_4$.

Table III. Kinetic Parameters for Reaction via Path B

T, °C	10^3K_3	10^4k_4, s^{-1}
160.0	1.85 ± 0.17	1.82 ± 0.09
165.0	2.26 ± 0.14	3.13 ± 0.07
170.0	2.53 ± 0.15	4.53 ● 0.07
175.0	2.38 ± 0.38	6.88 ± 0.27

$\Delta H_3°$ = 9.4 ± 2.9 kcal mol^{-1}
$\Delta S_3°$ = 9.2 ± 6.7 cal K^{-1} mol^{-1}

Table IV. Kinetic Parameters for Loss of CO from Some Os_3 Clusters

cluster	10^4k (125 °C), s^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal K^{-1} mol^{-1}
$Os_3(CO)_{12}$[a]	3.5	32.87 ± 0.28	7.6 ± 0.9
$Os_3(CO)_{11}(\eta^2\text{-}C_2Ph_2)$[b]	0.08	32.4 ± 1.8	−1.6 ± 4.3
$Os_3(CO)_{10}(\mu\text{-}C_2Ph_2)$[c]	340	28.04 ± 1.82	4.6 ± 5.1
$Os_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$[a]	2.5	39.3 ± 1.2	23.1 ± 3.1

[a] Data from ref 17 and 19. [b] See reaction 4. Reaction is concerted (see text). [c] See reaction 9.

$$Os_3(CO)_{12} + C_2Ph_2 \overset{K_3}{\rightleftharpoons} Os_3(CO)_{11}(\eta^2\text{-}C_2Ph_2) + CO \quad (3)$$

$$Os_3(CO)_{11}(\eta^2\text{-}C_2Ph_2) \xrightarrow{k_4} Os_3(CO)_{10}(\mu\text{-}C_2Ph_2) + CO \quad (4)$$

$$1/k_a = 1/k_4 + (1/K_3k_4)[CO]/[C_2Ph_2] \quad (5)$$

Values of K_3 and k_4 at various temperatures (Table III) lead to estimates of $\Delta H_3°$ and $\Delta S_3°$ (Table III) and $\Delta H_4^\ddagger$ and $\Delta S_4^\ddagger$ (Table IV).[21] The values of K_3, $\Delta H_3°$, and $\Delta S_3°$ show that the displacement of CO by C_2Ph_2 is energetically unfavorable because of the quite large and positive value of the enthalpy of reaction. This is likely to be a good measure of the different strengths of the Os–CO and Os–(C_2Ph_2) bonds, a conclusion supported qualitatively by the rapidity with which the C_2Ph_2 is displaceable, even at room temperature. Comparable data on the energetics of bonding of unsaturated hydrocarbons to carbonyl clusters are, unfortunately, not available.

Reaction 4 seems to involve a concerted displacement of CO. The absence of a term in $[CO]^2$ in eq 1b and 5 shows that reaction 4 is not retarded by [CO]. Reversible formation of $Os_3CO)_{10}(\eta^2\text{-}C_2Ph_2)$ followed by isomerization to $Os_3(CO)_{10}(\mu\text{-}C_2Ph_2)$ cannot, therefore, be occurring. The corresponding reaction of $Os_3(CO)_{11}(\eta^2\text{-}1\text{-decyne})$ is very much faster,[22] yet the nature of the η^2-alkyne should not have much effect on the rate of CO dissociation from another Os atom in the cluster. On the other hand, the greater steric effect of C_2Ph_2 might well inhibit a concerted displacement of CO and concurrent rearrangement of bonding of the alkyne to the Os_3 cluster. The concerted nature of reaction 4 is also suggested by the negative or, at most, only slightly positive value of $\Delta S_4^\ddagger$.

The data in Table IV show that the presence of the C_2Ph_2 substituent in $Os_3(CO)_{11}(\eta\text{-}C_2Ph_2)$ deactivates the cluster toward CO loss, compared with $Os_3(CO)_{12}$, by a factor of ca. 40 at 125

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(16) In all cases the dependences of k_A on $[C_2Ph_2]$ and of $1/k_B$ on $[CO]/[C_2Ph_2]$ were analyzed by a weighted linear least-squares program in which k_A and k_B were assumed to have characteristic probable errors (standard deviations), $\sigma(k_A)$ and $\sigma(k_B)$, expressed as a percentage. The initial estimates of the standard deviations were always adjusted upward, according to the number of degrees of freedom involved,[17] so that 95% confidence limits can be obtained by doubling the adjusted values.

(17) Poë, A. J.; Sekhar, V. C. Inorg. Chem. 1985, 24, 4376–4380.

(18) Estimated from activation parameters given in ref 17 and 19.

(19) Brodie, N. M. J.; Poë, A. J.; Sekhar, V. C. J. Chem. Soc., Chem. Commun. 1985, 1090–1091.

(20) The reverse of reaction 4 only occurs in the absence of C_2Ph_2.

(21) Each value of ln K_3 or ln (k_4/T) was weighted according to the inverse of its variance, as obtained from the standard deviations of K_3 and k_4 shown in Table III.

(22) Poë, A. J.; Smith, R. T., unpublished observations.

°C. This factor would presumably be larger if the loss of CO from the alkyne complex were not compensated for by the concerted adjustment of the bonding of the C_2Ph_2. If the value of $\Delta S^{\ddagger}$ for the nonassisted loss of CO is the same as that for $Os_3(CO)_{12}$,[17,19] then the value of $\Delta H^{\ddagger}$ for the nonassisted loss would have to be $\gtrsim$36 kcal mol^{-1} for this process to be negligible compared with assisted loss. This value is considerably larger than that for $Os_3(CO)_{12}$. This deactivation is similar to that brought about by one P-*n*-Bu_3 substituent[17,19] (Table IV).

Although metal carbonyl clusters in general,[23] and $Os_3(CO)_{12}$ in particular,[17,19] are known to be susceptible to nucleophilic attack by σ-donor ligands, direct attack on a coordinatively saturated complex by an alkyne, as indicated by eq 2, has not been observed before. It is only detected here because of the extreme slowness of the CO-retarded reaction. Bimolecular reaction with P-*n*-Bu_3 leads directly to fragmentation of the Os_3 cluster,[17] and it is likely that attack by C_2Ph_2 also causes fragmentation. It cannot lead to simple substitution since the $Os_3(CO)_{11}(\eta^2\text{-}C_2Ph_2)$ produced would immediately revert to $Os_3(CO)_{12}$ at the high [CO] used. Concerted displacement of two CO ligands seems unlikely. On the other hand, $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-alkene})$ and $Os(CO)_4(\eta^2\text{-alkene})$ are known[24] products of photolysis of $Os_3(CO)_{12}$ with alkenes, and it is perfectly possible that alkyne analogues could be formed as initial products of the thermal reactions. How they subsequently react to form the final products is not shown by the kinetic data. Although not very precise, the activation parameters (Table III) for the minor path governed by k_{A2} suggest that the bonding within the $Os_3(CO)_{12}$ has been greatly weakened in forming the $Os_3(CO)_{12}{\cdot}C_2Ph_2$ transition state.

The least important path, governed by k_{A1}, is not easy to characterize mechanistically. It cannot be caused by reaction with impurities specifically in the decalin because a small intercept is also shown by reactions in tetradecane under 100% CO at 190 °C. It is conceivable that it involves an initial rate-determining isomerization of $Os_3(CO)_{12}$, as in eq 6, to a form that can very readily be attacked by C_2Ph_2 (eq 7). Photolysis of $Os_3(CO)_{12}$

$$Os_3(CO)_{12} \xrightarrow{k_{A1}} Os_3(CO)_{12}^{*} \qquad (6)$$

$$Os_3(CO)_{12}^{*} + C_2Ph_2 \xrightarrow{\text{fast}} \text{fragmentation} \qquad (7)$$

produces a reactive isomer that undergoes bimolecular fragmentation on attack by alkenes.[25] However, the absence of any substantial dependence of k_{A1} on temperature is surprising, and the mechanism of this relatively minor path remains in doubt.

Reaction of $Os_3(CO)_{10}(C_2Ph_2)$. Reactions with C_2Ph_2 under N_2 at 80–95 °C were accompanied by the growth of bands (Table I) due to $Os_3(CO)_9(C_4Ph_4)$, and these were subsequently replaced by bands due to $Os_3(CO)_8(C_4Ph_4)$. In the presence of CO, only bands due to the former complex were observed to grow, and they subsequently disappeared and were replaced by bands due to $Os_2(CO)_6(C_4Ph_4)$ together with weak bands assignable[26] to $Os(CO)_5$. No bands due to $Os_3(CO)_{12}$ were observed during or after these latter reactions. $Os_3(CO)_{10}(C_2Ph_2)$ is found to convert to $Os_3(CO)_{12}$ only in the absence of C_2Ph_2 and under CO at temperatures above ca. 125 °C. The values of k_{obsd} (Table V) for loss of $Os_3(CO)_{10}(C_2Ph_2)$ at 85 °C were found to depend on [CO] and [C_2Ph_2] according to eq 8. This is identical in form with

$$1/k_{obsd} = c + d[CO]/[C_2Ph_2] \qquad (8)$$

eq 2, and values of *c* and *d* are shown in Table V. The temperature dependence of values of k_{obsd} under N_2 gave the activation parameters in Table IV.

Table V. Rate Data for Reaction of $Os_3(CO)_{10}(\mu\text{-}C_2Ph_2)$ with C_2Ph_2 in Decalin[a]

T, °C	[C_2Ph_2], M	10^4[CO], M	$10^4 k_{obsd}$, s^{-1}
80.0	0.064	0[b]	3.40
85.0	0.011	2.73	0.78
85.0	0.022	2.73	1.25
85.0	0.064	0[b]	5.70
85.0	0.064	2.73	3.10
85.0	0.064	13.7	0.83
85.0	0.064	21.8	0.46
90.0	0.064	0[b]	10.0
95.0	0.064	0[b]	18.0

At 85 °C: $c = 1627 \pm 112$ s $d = (4.85 \pm 0.52) \times 10^5$ s

[a] The parameters *c* and *d* are defined in eq 8. [b] Reactions under N_2. Other reactions were carried out under CO–N_2 mixtures of known composition.

This reaction can be concluded to proceed via the steps shown in eq 9–11. Reactions 9 and 10 represent a simple, slow, CO dissociative substitution reaction, and reaction 11 involves combination of the two differently bonded C_2Ph_2 moieties in $Os_3(CO)_9(\mu\text{-}C_2Ph_2)(\eta^2\text{-}C_2Ph_2)$ to form the osmacyclopentadiene product II. The scheme implies that $c = 1/k_9$ and $d/c = k_{-9}/k_{10}$.

$$Os_3(CO)_{10}(\mu\text{-}C_2Ph_2) \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} Os_3(CO)_9(\mu\text{-}C_2Ph_2) + CO \qquad (9)$$

$$Os_3(CO)_9(\mu\text{-}C_2Ph_2) + C_2Ph_2 \xrightarrow{k_{10}} Os_3(CO)_9(\mu\text{-}C_2Ph_2)(\eta^2\text{-}C_2Ph_2) \qquad (10)$$

$$Os_3(CO)_9(\mu\text{-}C_2Ph_2)(\eta^2\text{-}C_2Ph_2) \xrightarrow{\text{fast}} Os_3(CO)_9(\mu\text{-}C_4Ph_4) \qquad (11)$$

This is confirmed by measurements of the rates of reaction 12.[28] These are independent of [PPh_3] and are governed by a first-order rate constant of (7.23 ± 0.16) × 10^{-4} s^{-1} at 85 °C which is in close

$$Os_3(CO)_{10}(\mu\text{-}C_2Ph_2) + PPh_3 \rightarrow Os_3(CO)_9(PPh_3)(\mu\text{-}C_2Ph_2) + CO \qquad (12)$$

agreement with the corresponding value of $1/c$ ((6.15 ± 0.30) × 10^{-4} s^{-1}). The complex $Os_3(CO)_9(\mu\text{-}C_2Ph_2)(\eta^2\text{-}C_2Ph_2)$ has been postulated to be formed in solution via the very reactive intermediate, $Os_3(CO)_9(\mu\text{-}C_2Ph_2)$, and to isomerize to $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ on "slight warming".[5] The values of k_{obsd} found under N_2 can, therefore, be equated with values of k_9, so the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in Table IV can be assigned to $\Delta H_9^{\ddagger}$ and $\Delta S_9^{\ddagger}$.

The dissociation of CO from $Os_3(CO)_{10}(\mu\text{-}C_2Ph_2)$ is ca. 4 × 10^3 times faster than from $Os_3(CO)_{11}(\eta^2\text{-}C_2Ph_2)$ at 125 °C (Table IV), so the ***bridging*** alkyne is a highly labilizing ligand compared with the terminal one. This suggests that the CO is probably not lost from the $Os(CO)_3$ moiety that is π-bonded to the C=C bond in I but that it is lost from one of the Os atoms that are σ bonded to the C=C unit. Metal–C σ bonds are known to be quite labilizing.[29] The loss is more likely to occur from the $Os(CO)_4$ moiety because this could be compensated for by formation of an Os=Os double bond and this would account for the rather low value of $\Delta S^{\ddagger}$. This could also explain why attack on the $Os_3(CO)_9(\mu\text{-}C_2Ph_2)$ intermediate by C_2Ph_2 is ca. 300 times slower than by CO,[30] the intermediate being coordinated to six other atoms and sterically very inaccessible to a rather large ligand like C_2Ph_2. It is interesting that the coupling of the two C_2Ph_2 units in $Os_3(CO)_9(\mu\text{-}C_2Ph_2)(\eta^2\text{-}C_2Ph_2)$ is such a fast reaction.[5]

Reaction of $Os_3(CO)_9(C_4Ph_4)$. Reaction of this complex, at room temperature and above, and in the presence of CO and C_2Ph_2, leads to the growth of IR bands due to $Os_2(CO)_6(C_4Ph_4)$ (Table I) and $Os(CO)_5$.[26] Even at room temperature, the bands

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[30] This ratio is given by k_{10}/k_{-9}, i.e., c/d in Table V.

Table VI. Rate Data for Reaction of $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ with CO in Decalin

T, °C	$[C_2Ph_2]$, M	10^3[CO], M	$10^4 k_{obsd}$, s^{-1}	k_{obsd}/[CO], M^{-1} s^{-1}
50.0	0.064	0.86	4.4	0.51
50.0	0.064	1.44	6.42[a]	0.45
50.0	0.005–0.100	2.30	7.96[b]	0.35
50.0	0.064	4.08	15.6	0.38
50.0	0.064	5.75	22.0	0.38
55.0	0.064	2.28	10.0	0.44
60.0	0.050	2.26	12.0	0.53
65.0	0.050	2.24	15.0	0.67
70.0	0.050	2.22	20.0	0.90

$\Delta H^* = 8.20 \pm 1.28$ kcal mol^{-1} [c] $\Delta S^* = -35.3 \pm 3.9$ cal K^{-1} mol^{-1} [c]

[a] Mean of five values with initial values of [complex] varied from 1×10^{-4} to 7×10^{-4} M. [b] Mean of five values. [c] Activation parameters from the dependence of ln (k_{obsd}/[CO]T) on $1/T$.

Table VII. Activation Parameters for Bimolecular Reaction of CO with Some Metal Carbonyl Clusters

cluster	ΔH^*, kcal mol^{-1}	ΔS^*, cal K^{-1} mol^{-1}
$Os_3(CO)_9(\mu\text{-}C_4Ph_4)$	8.2 ± 1.3	−35.3 ± 3.9
$H_2Ru_4(CO)_{13}$[a]	12.5 ± 0.5	−36.6 ± 1.6
$H_2FeRu_3(CO)_{13}$[a]	20.0 ± 2.0	−25.4 ± 5.8

[a] Reference 32.

due to $Os(CO)_5$ eventually disappear, leaving $Os_2(CO)_6(C_4Ph_4)$ as the only product, its IR bands increasing in intensity as those due to $Os(CO)_5$ decrease. Reaction of $Os_3(CO)_9(C_4Ph_4)$ with PPh_3 at room temperature was found to lead to $Os_2(CO)_6(C_4Ph_4)$ and $Os(CO)_4(PPh_3)$. The kinetics of reaction with CO were followed at 50–70 °C and values of k_{obsd} found to be independent of the concentrations of reacting complex or C_2Ph_2 but linearly dependent on [CO] (Table VI). The mean value of k_{obsd}/[CO] at 50.0 °C is 0.41 ± 0.04 M^{-1} s^{-1}. Activation parameters for this second-order fragmentation reaction are also shown in Table VI.

The absence of any dependence on [complex] precludes spontaneous reversible fragmentation into $Os_2(CO)_5(\mu\text{-}C_4Ph_4)$ and $Os(CO)_4$ followed by weakly competing addition of CO. Such a process would be half order in $[Os_3(CO)_9(\mu\text{-}C_4Ph_4)]$.[31] Fragmentation most probably occurs by F_N2 attack[17,19] by CO at the $Os(CO)_4$ moiety since reaction with PPh_3 leads to $Os(CO)_4(PPh_3)$ very much more rapidly in accord with the much higher nucleophilicity of PPh_3. It is interesting that the $Os(CO)_5$ product appears to react with C_2Ph_2, under these mild conditions, to form $Os_2(CO)_6(\mu\text{-}C_4Ph_4)$.

The activation parameters are typical of other bimolecular reactions of carbonyl clusters.[23] Activation parameters for the bimolecular reaction of CO with $H_2Ru_4(CO)_{13}$ and $H_2FeRu_3(CO)_{13}$[32] are compared with those of $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ in Table VII. The former reactions lead to fragmentation, formation of $Ru(CO)_5$ and $Fe(CO)_5$ resulting from nucleophilic attack at an $M(CO)_4$ moiety. However, these reactions are believed to go via initial formation of a "butterfly" cluster $H_2M_4(CO)_{14}$ which subsequently undergoes fragmentation, probably via further CO attack. Immediate fragmentation after attack by the first CO is unlikely because of the highly unsaturated nature of the residual $H_2M_3(CO)_9$ that would be formed in addition to $M(CO)_5$. The case of $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ is quite different in that a very small change in the bonding of the osmacyclopentadiene ring is expected and the two single Os–Os bonds to the displaced $Os(CO)_4$ group can be replaced smoothly by formation of an Os═Os double bond in the remaining $Os_2(CO)_5(\mu\text{-}C_4Ph_4)$. This species would be in accord with the 18-electron rule but, being unsaturated, would be expected to react rapidly with another CO to form $Os_2(CO)_6(\mu\text{-}C_4Ph_4)$. The much lower value of ΔH^* for fragmentation of the Os_3 cluster can then be readily understood.

Summary. This kinetic study has revealed the mechanistic and energetic details of how a simple binary carbonyl cluster can react sequentially with an alkyne to form a series of derivatives. The initial reaction of the cluster proceeds via two main mechanisms: one involving a labile substitutional preequilibrium; the other an unexpected and unique bimolecular attack by the alkyne that leads directly to fragmentation.

Intermediate complexes formed by substitution reactions can react via CO dissociative paths. In one of these the loss of CO is assisted by a concerted rearrangement of a two-electron donor alkyne to a four-electron donor form. In the other, a simple reversible CO dissociation is accelerated by the presence of Os—C σ bonds and assisted by formation of an Os═Os double bond. Finally, an organometallic Os_3 derivative undergoes nucleophilic (F_N2) attack by CO during which an $Os(CO)_4$ moiety is selectivity and cleanly removed from the cluster in a very low energy process. It remains to be seen how general this mechanistic diversity is, but is seems to us to be most probably a characteristic feature of such reactions.

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Registry No. $Os_3(CO)_{12}$, 15696-40-9; C_2Ph_2, 501-65-5.

Supplementary Material Available: Tables of kinetic data of reactions of $Os_3(CO)_{12}$ with C_2Ph_2 in decalin (3 pages). Ordering information is given on any current masthead page.

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