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Alkyne Ligand Enhancement of the Substitution Lability of Mononuclear Osmium, Ruthenium, and Iron Carbonyls

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Abstract: The kinetic influence of an alkyne ligand, hexafluorobut-2-yne (HFB), has been investigated by studying the reactions of phosphines (PR_3) with the complexes $M(CO)_4(\eta^2\text{-HFB})$ (M = Fe, Ru, Os). The rate of production of $M(CO)_3(PR_3)(\eta^2\text{-HFB})$ is independent of the nature and concentration of the phosphine in all cases, indicating that the rate-controlling step is CO dissociation. The kinetic parameters, k_1 (s^{-1}, 25 °C), ΔH^* (kJ mol^{-1}), and ΔS^* (cal mol^{-1} K^{-1}) are: 9.5, 88.2 ± 2.3, 70 ± 10 (Fe); 1.25×10^{-2}, 103.6 ± 2.4, 66 ± 8.6 (Ru); 3.5×10^{-3}, 99.5 ± 0.8, 21 ± 2.7 (Os). When the rate constants at 25 °C for $M(CO)_4(\eta^2\text{-HFB})$ are compared to those of the parent $M(CO)_5$, the ratios are $\sim 3 \times 10^{13}$, 1.8×10^2 and 1×10^7 for M = Fe, Ru, and Os, respectively. Clearly the alkyne increases the substitution lability, and the effect is spectacular with Fe, very large with Os, and substantial but relatively more modest with Ru. The increased lability results mainly from a reduced ΔH^* of ~80, 10, and 33 kJ mol^{-1} for Fe, Ru, and Os, respectively, and this is attributed largely to stabilization of the transition state by 4-electron donation from the alkyne ligand. Also reported are kinetics of formation of some trans $M(CO)_2(PR_3)_2(\eta^2\text{-HFB})$ complexes and an extension of earlier work on the $Os(CO)_5/PPh_3$ system.

Introduction

Transition-metal carbonyls are one of the most important classes of organometallic complexes.[1] They serve as useful starting materials for other organometallic complexes,[2] as stoichiometric reagents in numerous organic transformations, and as catalyst precursors for important catalytic processes.[3] Because the transition-metal carbonyls normally are saturated 18-electron species, they tend to be kinetically inert and a challenge in the field has been to discover new methods to bring about CO substitution.

Several reagents are known to promote removal of CO ligands. For example, Me_3NO can oxidize CO to CO_2 and the latter is readily lost and replaced by other ligands.[4] Other promoters of CO elimination that have been used include R_3PO,[5] KOMe,[6] KH, and $NaBH_4$.[7] Another approach is to use electron-transfer reagents, including supported transition metals, to generate labile 17- or 19-electron species.[8] Although useful, these processes are by no means universal in their application.

In addition to external reagents, spectator ligands on metal carbonyl derivatives also can faciltate CO substitution through steric and electronic effects. Well-known examples of this phenomenon are the trans-effect[9] and cis-labilization.[10,11]

Recent reports from our laboratories[12] on the synthesis and reactivity of $M(CO)_4(\eta^2\text{-RC}{\equiv}\text{CR})$ (M = Ru, Os) complexes indicate that these are remarkably reactive species. For example, with M = Os and R = H, CO exchange is complete in 1 h at 0−10 °C. These compounds also appear to act as electrophiles in unusual reactions with other 18-electron metal carbonyls to give a variety of dimetallacyclic products.

The present kinetic study was undertaken to elucidate the mechanism of substitution on $M(CO)_4(\eta^2\text{-HFB})$ (M = Fe, Ru,

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Scheme 1

$$\mathrm{M(CO)_4(\eta^2\text{-}HFB) + PR_3 \xrightarrow{k_1} M(CO)_3(PR_3)(\eta^2\text{-}HFB) + CO}$$

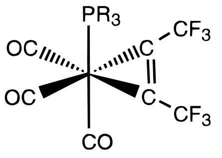
$$\mathrm{M(CO)_3(PR_3)(\eta^2\text{-}HFB) + CO \xrightarrow{k_2} M(CO)_2(PR_3)_2(\eta^2\text{-}HFB) + CO}$$

Os; HFB = hexafluorobut-2-yne) complexes and to quantify the labilizing effect of the alkyne ligand by comparison to their $M(CO)_5$ parents. The results provide further data for comparisons of periodic trends in reactivity for metal carbonyl systems. It is known that the order of reactivity for the $M(CO)_5$ systems is Ru $\gg$ Os $>$ Fe. It is shown here that the alkyne ligand dramatically changes this order to Fe $\gg$ Ru $>$ Os and the $Fe(CO)_4(\eta^2\text{-alkyne})$ system undergoes a spectacular 13 orders of magnitude increase in substitution rate compared to $Fe(CO)_5$.

Results

The general reaction system is shown in Scheme 1. The formation of the mono- and bisphosphine complexes has been observed primarily by infrared spectroscopy. For many of the phosphines studied, both k_1 and k_2 could be determined, but with some, k_2 was so large relative to k_1 that only the latter could be measured. The kinetics with various phosphines has been explored mainly with M = Os.

Reactions with $Os(CO)_4(\eta^2\text{-HFB})$. Synthetic studies[13] have allowed the characterization of some representative intermediate and final products of phosphine substitution in this system. The $^{13}C\{^1H\}$ NMR shows that the mono- and disubstituted phosphine derivatives correspond to the axial and diaxial, trans isomers as shown in **I** and **II**, respectively.



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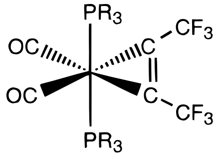

II

If two or more equivalents of PMe_3 or PPh_3 are used, the product isolated is $Os(CO)_2(PR_3)_2(\eta^2\text{-HFB})$ (R = Me, Ph), and the ^{19}F and $^{13}C\{^1H\}$ NMR spectra show that this species is the trans phosphine isomer **II**. This observation also demonstrates that compounds **II** are resistant to further substitution by phosphine ligands.

For this system, a wide range of phosphines have been studied and in many cases both substitution steps can be kinetically characterized. The variation of k_2 with phosphine illustrates some aspects of the influence of phosphines as a spectator ligands.

The kinetics of the reactions have been monitored by infrared spectroscopy, using both reactant and product bands to determine the rate constants. The reactant $Os(CO)_4(\eta^2\text{-HFB})$ is characterized by strong bands at 2070 and 2028 cm^{-1}, while the $Os(CO)_3(PR_3)(\eta^2\text{-HFB})$ derivatives have bands at about 2083−2097, 2008−2013, and 1980−1998 cm^{-1}. The final products, $Os(CO)_2(PR_3)_2(\eta^2\text{-HFB})$, have characteristic bands in the 1984−2034 and 1912−1970 regions. Details for each compound are given in the Supporting Information. Bodner et al.[14] determined the ^{13}C chemical shift parameter (δ, ppm) for a series of $Ni(CO)_3(PR_3)$ compounds and suggested δ as an electronic effect parameter for phosphine ligands. It is noteworthy that the carbonyl stretching frequencies for the $Os(CO)_{4-n}(PR_3)_n(\eta^2\text{-HFB})$ species give a good linear correlation with δ. The ν_{CO} values decrease with increasing δ as expected if a larger δ reflects greater σ-donor strength of PR_3 and therefore greater π back-bonding to CO.

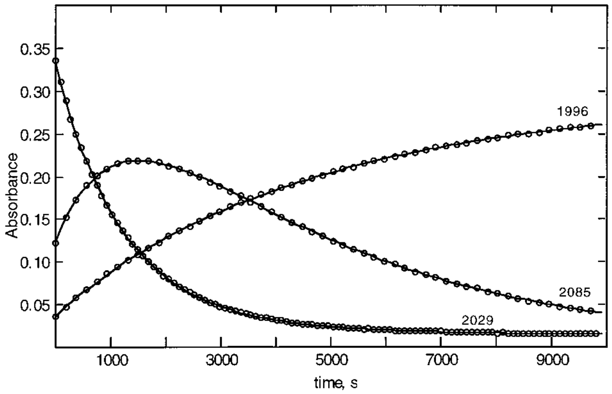

Figure 1. Absorbance−time variation for the reaction of 0.10 M PMe_3 with $Os(CO)_4(\eta^2\text{-HFB})$ at 14.6 °C in dichloromethane. Numbers indicate the monitoring wavenumber; circles are experimental points, and curves are least-squares fits to a biphasic model.

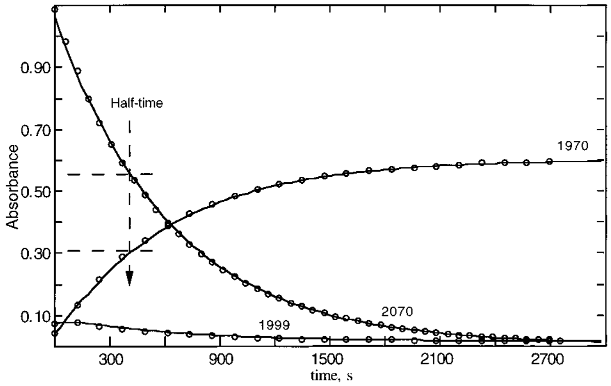

Figure 2. Absorbance−time variation for the reaction of 0.10 M $P(OPh)_3$ with $Os(CO)_4(\eta^2\text{-HFB})$ at 20.0 °C in dichloromethane. Numbers indicate the monitoring wavenumber; circles are experimental points, and curves are least-squares fits to a biphasic model.

The reaction may be monitored in several complementary ways. The disappearance of reactant monitored at 2070 or 2028 cm^{-1} allows k_1 to be determined with little interference from the second step. The growth and decay of **I** can be observed at ~2010 or 2090 cm^{-1}, while **II** can be observed in the 1930 or 2000 cm^{-1} regions. Examples of absorbance−time curves are shown in Figure 1 for the reaction with PMe_3. Least-squares fits of this type of data to a biphasic model allowed values of the first-order rate constants k_1 and k_2 to be determined. The conformance to a first-order rate law indicates that the buildup of CO to ~ 4 mM during the reaction causes no inhibition of the rate. For some systems, k_2 could not be evaluated because it is so large, relative to k_1, that the first step is entirely rate controlling. An example of this behavior is shown for triphenyl phosphite in Figure 2. The small absorbance at 1999 cm^{-1} indicates that very little **I** is present, and the half-time for disappearance of reactant (2070 cm^{-1}) and formation of product **II** (1970 cm^{-1}) are essentially identical, as shown by the dashed lines on Figure 2.

In principle, the rate constants k_1 and k_2 are pseudo-first-order because the phosphine or phosphite concentration (>0.04 M) was always larger than that of $Os(CO)_4(\eta^2\text{-HFB})$ ($<1\ \times$

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Table 1. Some PR_3 Properties and Rate Constants for Reactions with $Os(CO)_4(\eta^2\text{-HFB})$ (k_1) and $Os(CO)_3(PR_3)(\eta^2\text{-HFB})$ (k_2)[a]

PR_3	temp, °C	pK_a[b]	δ[c], ppm	cone angle,[d] deg	E'_R (E_R),[e] kcal mol^{-1}	10^4k_1, s^{-1}	10^4k_2, s^{-1}
PMe_3	14.5	8.65	5.05	118	26 (39)	8.54	2.50
PMe_2Ph	14.6	6.5	4.76	122	33 (44)	8.58	2.16
$PMePh_2$	14.8	4.57	4.53	136	39 (57)	9.11	3.44
PPh_3	14.3	2.73	4.30	145	43 (75)	7.33	9.02
PPh_3	14.3	2.73	4.30	145	43 (75)	4.09^f	10.7^f
PPh_3	14.3	2.73	4.30	145	43 (75)	8.70^g	10.6^g
PPh_3	14.3	2.73	4.30	145	43 (75)	9.69^h	7.05^h
$P(p\text{-tolyl})_3$	14.8	3.84	4.50	145	43 (75)	8.11	12.0
PEt_3	14.7	8.69	5.54	132	44 (61)	8.46	10.6
$P(OMe)_3$	14.8	2.6	3.18	107	48 (52)	8.29	38.7
PCy_3	15.5	9.7	6.32	170	67 (116)	8.97	fast
$P(OPh)_3$	14.3	−2.0	1.69	128	72 (65)	7.99	fast

[a] The solvent is dichloromethane unless otherwise indicated. [b] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. [c] The ^{13}C NMR chemical shift of $Ni(CO)_3(PR_3)$ relative to $Ni(CO)_4$ given in ref 14. [d] Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981. [e] Ligand repulsive energies for $CpRh(CO)(L)$ (E_R') and $Cr(CO)_5(L)$ (E_R) from: Choi, M.-G; Brown, T. L. *Inorg. Chem.* **1993**, *32*, 5603. Revised values for PMe_2Ph and $PMePh_2$ have been provided by Professor Brown. [f] In THF. [g] In toluene. [h] In Decalin.

10^{-3} M). However, it was found that the rates for all of the reactions are independent of the concentration of the phosphine or phosphite. This feature was established for concentrations of triphenylphosphine between 0.043 and 0.25 M in dichloromethane (DCM) and typically was checked for other systems between 0.1 and 0.2 M. Therefore, the rate law for both steps is given by

$$\text{rate} = k_i[Os(CO)_4(\eta^2\text{-HFB})] \qquad (1)$$

where $i = 1$ or 2. Furthermore, the value of k_1 was found to be independent of the nature of the phosphine or phosphite, even though these had a wide range of basicities and steric requirements. However, k_2 does depend on the nature of the phosphine or phosphite, but this is not unexpected because the P-donor ligand, already present as a spectator ligand in **I**, will affect its reactivity.

The solvent dependence of the reactions with PPh_3 was explored by studies in THF, toluene, and decalin, in addition to the most often used solvent, dichloromethane (DCM).

The results for various phosphines are given in Table 1 and activation parameters are summarized in Table 3. Full details are given in the Supporting Information.

Reaction of $Os(CO)_5$ with PPh_3. This study was undertaken to permit comparison of the reactivity of $Os(CO)_5$ and $Os(CO)_4(\eta^2\text{-HFB})$. The reaction has been studied previously by Basolo and co-workers,[15] but it has been noted[16] that the results appear anomalous because the ΔS^* is some 60 J mol^{-1} K^{-1} smaller than for the Fe and Ru analogues. Since this system makes an important point of comparison, it seemed worthwhile to study it again. Basolo and co-workers used a batch method and analyzed for disappearance of $Os(CO)_5$ at 1993 cm^{-1} in Decalin, and found that the rate was independent of the concentration and nature of the phosphine. We have studied the reaction with PPh_3 in Decalin by continuous monitoring with the sample heated in the same infrared cell used for the $Os(CO)_4(\eta^2\text{-HFB})$ study. For the determination of the rate constants, the disappearance of $Os(CO)_5$ at 2034 and 1991 cm^{-1} and appearance of $Os(CO)_4(PPh_3)$ at 1943 cm^{-1} and $Os(CO)_3(PPh_3)_2$ at 1899 cm^{-1} were used to determine k_1 and k_2. Formation of the latter product was indicated also by the decrease of absorbance at 1943 cm^{-1} for long reaction times. The infrared bands of the phosphine derivatives are consistent with previous reports[17] and with axial phosphine ligands in an overall trigonal bipyramidal structure.

Table 2. Kinetic Results for Reaction of PPh_3 with $Os(CO)_5$ in Decalin

[PPh_3], M	temp, °C	10^5k_1, s^{-1}	10^5k_2, s^{-1}	ref
0.15	115.4	11.9	1.23	this work
0.15	110.0	6.10	0.60	this work
0.15	109.6	6.42	0.54	this work
0.15	100.0	1.96	0.138	this work
0.019−0.112	96.0	1.05^a		Basolo et al.
0.15	90.2	0.662		this work
0.15	90.0	0.586		this work
0.037−0.075	86.0	0.33^a		Basolo et al.
0.0335	76.4	0.10		Basolo et al.

[a] Average of values reported at different [PPh_3].

The results for this system are summarized in Table 2 and activation parameters are given in Table 3. The k_1 is well defined by the disappearance of $Os(CO)_5$, and our values agree with those of Basolo and co-workers[15] as shown by the temperature-dependence plot of data from both studies in Figure 3. Since it was not practical to follow the reaction to completion, k_2 is less certain and was evaluated by holding k_1 fixed during the least-squares analysis of the data at 1943 and 1899 cm^{-1}. The resulting k_2's do give a satisfactory temperature plot, also shown in Figure 3.

Reactions with $Ru(CO)_4(\eta^2\text{-HFB})$. Synthetic studies[13] have shown that the final product in the presence of excess phosphine is the Ru analogue of **II**. With PPh_3, the disappearance of reactant at 2074 and 2042 cm^{-1} and appearance of product at 2010 and 1949 cm^{-1} were monitored, and the PPh_3 concentration was varied from 0.10 to 0.25 M. For $P(OPh)_3$ and PCy_3 the 2042-cm^{-1} peak could not be used because it is also present in the product, and product formation was observed at 1984 cm^{-1}.

The kinetic behavior and rate law for $Ru(CO)_4(\eta^2\text{-HFB})$ are the same as for $Os(CO)_4(\eta^2\text{-HFB})$ except that k_2 was too large to be evaluated for PPh_3 as well as for $P(OPh)_3$ and PCy_3. The results are summarized in Table 4.

Reactions with $Fe(CO)_4(\eta^2\text{-HFB})$. With the recent availability of this compound,[18] it was of obvious interest to study its phosphine substitution reactivity in order to complete the triad comparison with the analogous Ru and Os compounds. Preliminary studies indicated that the reaction of $Fe(CO)_4(\eta^2\text{-HFB})$ with PPh_3 is much faster than that of either $Os(CO)_4(\eta^2\text{-HFB})$ or $Ru(CO)_4(\eta^2\text{-HFB})$ and is too fast to study by our infrared system, even at −20 °C. Therefore, ^{19}F NMR monitoring has been used to study the reaction in the −30 to −40 °C range with the disappearance of reactant being observed at −55.8 ppm.

The first substitution with PPh_3 gives the axial isomer with structure **I**, and the second substitution results in the diaxial isomer **II**, mirroring the Ru and Os behavior. However, with Fe, the second substitution is not complete and an equilibrium is established between **I** and **II** as the concentration of dissociated CO builds up in the sealed NMR tube. An unanticipated result with the bulky PCy_3 ligand is that monosubstitution step gives not only the axial isomer **I** but also the equatorial isomer. Further reaction to give the disubstituted

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Table 3. Kinetic Results for Substitution Reactions on $Os(CO)_4(L)$ (k_1) and $Os(CO)_3(PR_3)(L)$ (k_2)

PR_3	(L)	solvent	temp range, °C	ΔH_1^*, kJ mol^{-1}	ΔS_1^*, J mol^{-1} K^{-1}	ΔH_2^*, kJ mol^{-1}	ΔS_2^*, J mol^{-1} K^{-1}
PPh_3	(η^2-HFB)	DCM	3.0−23.6	99.5 ± 0.8	41.8 ± 2.7	99.4 ± 1.6	43.2 ± 5.6
PPh_3	(η^2-HFB)	THF	3.0−23.6	98.3 ± 1.3	32.7 ± 4.4	95.6 ± 1.9	30.6 ± 6.5
$P(OPh)_3$	(η^2-HFB)	DCM	3.0−23.6	96.1 ± 2.6	30.5 ± 8.9		
PCy_3	(η^2-HFB)	DCM	10.6−24.1	99.3 ± 1.0	41.2 ± 3.6		
PPh_3	(CO)[b]	DEC	90−115	133.4 ± 2.6	20.8 ± 7.0	168 ± 2.9[c]	92 ± 7.5[c]

[a] The solvents are: DCM, dichloromethane; THF, tetrahydrofuran; DEC, Decalin; ΔH^* and ΔS^* are given to an additional figure to avoid round-off errors in recalculation, and error limits are one standard deviation. [b] See Table 2 for details. [c] k_2 could only be evaluated between 100 and 115 °C.

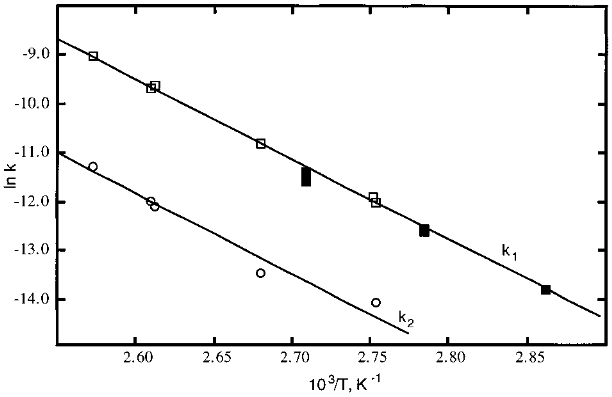


Figure 3. Temperature dependence of the reaction of PPh_3 with $Os(CO)_5$ (k_1) and $Os(CO)_4(PPh_3)$ (k_2) in Decalin; (□, ○), results from this study; (■) results from Basolo and co-workers, ref 20.

compound with structure **II** is observed under synthetic conditions when CO does not build up in the system, but this step is not observed in the sealed NMR tube used for the kinetic studies. Full details of the nature of these products will be the subject of a forthcoming publication, and only the kinetics of the disappearance of reactant in the first substitution step will be considered here.

The general kinetic behavior for the k_1 step is the same as for the other systems. The rate of CO displacement is independent of the concentration and nature of the phosphine (PPh_3, PCy_3, and $P(OPh)_3$). The first-order rate constants are summarized in Table 5. The activation parameters, determined from the temperature dependence of k_1, are given in Table 6.

Discussion

All of the systems studied here show rates that are independent of the concentration and nature of the entering group and are consistent with the usual dissociative mechanism shown in Scheme 2. This is also indicated by the positive ΔS^* values.

With a steady-state assumption for the concentration of the dissociative intermediate, this mechanism predicts that the observed rate constant (k_1 or k_2) should be given by

$$k_{\mathrm{i}} = k_{\mathrm{id}}k_{\mathrm{is}}[PR_3]/k_{-\mathrm{id}}[CO] + k_{\mathrm{is}}[PR_3] \qquad (2)$$

and under our experimental conditions of $[PR_3] \gg [CO]$, the observations indicate that $k_{\mathrm{is}}[PR_3] \gg k_{-\mathrm{id}}[CO]$ so that eq 2 reduces to eq 3.

$$k_{\mathrm{i}} = k_{\mathrm{id}} \qquad (3)$$

Therefore, the results in Tables 1, 3, 4, and 5 give the kinetic parameters related to k_{id} for CO dissociation from $Os(CO)_4(\eta^2\text{-HFB})$, $Ru(CO)_4(\eta^2\text{-HFB})$, and $Fe(CO)_4(\eta^2\text{-HFB})$, respectively. With obvious modifications, Scheme 2 also can apply to substitution on $Os(CO)_5$, and the results in Table 2 relate to CO dissociation from this species.

Table 4. Kinetic Results for Reactions of PR_3 with $Ru(CO)_4(L)$ Compounds[a]

PR_3	(L)	k, s^{-1}		ΔH,* kJ mol^{-1}	ΔS,* J mol^{-1} K^{-1}
		6.5 °C	25 °C		
PPh_3	(η^2-HFB)[b]	7.5×10^{-4}	1.25×10^{-2}	103.6 ± 2.4	66.0 ± 8.6
$POPh_3$	(η^2-HFB)	8.2×10^{-4} [c]	(1.3×10^{-2})[d]		
PCy_3	(η^2-HFB)	7.3×10^{-4} [c]	(1.3×10^{-2})[d]		
PPh_3	CO[e]		73×10^{-6}	115.6	63.6
	PPh_3[f]		3.2×10^{-6}	125.9	72.4
	PCy_3[f]		29×10^{-6}	115.9	56.9
	$PMePh_2$[f]		1.3×10^{-6}	124.3	59.0
	$P(OEt)_3$[f]		0.43×10^{-6}	129.7	68.2
P^nBu_3	P^nBu_3[g]		0.45×10^{-6}	132.1	76.6

[a] The solvent is DCM unless otherwise indicated. [b] Temperature range is 1.8−15.8 °C; errors are one standard deviation. [c] Experimental rate constants at temperatures of 6.8 and 6.2 °C for $P(OPh)_3$, and PCy_3, respectively. [d] Calculated assuming the ΔH^* for PPh_3. [e] From Huq, R.; Poë, A. J.; Chawla, S. *Inorg. Chim. Acta* **1980**, *38*, 121, in cyclohexane over a temperature range of 30−50 °C. [f] With various entering groups, in Decalin (PPh_3, $PMePh_2$) and heptane (PCy_3, $P(OEt)_3$) as given by: Chen, L.; Poë, A. J. *Inorg. Chem.* **1989**, *28*, 3641. [g] Poë, A.; Twigg, M. V. *Inorg. Chem.* **1974**, *13*, 2982, in Decalin.

Table 5. Kinetic Results for Reactions of PR_3 with $Fe(CO)_4(\eta^2\text{-HFB})$ in CD_2Cl_2[a]

PR_3	temp, °C	$[PR_3]$, M	10^3k_1, s^{-1} [b,c]
PPh_3	−30.7	0.20	2.16 ± 0.06 (2.19)
PCy_3	−33.5	0.30	1.34 ± 0.05 (1.30)
$P(OPh)_3$	−33.5	0.30	1.22 ± 0.05 (1.30)
PPh_3	−33.5	0.30	1.30 ± 0.03 (1.30)
PPh_3	−33.7	0.20	1.28 ± 0.05 (1.25)
PPh_3	−33.7	0.10	1.30 ± 0.05 (1.25)
PPh_3	−36.7	0.20	0.694 ± 0.03 (0.704)
PPh_3	−39.9	0.20	0.375 ± 0.07 (0.375)

[a] Rate constants determined by ^{19}F NMR monitoring of the disappearance of the singlet at δ −56.0 ppm in a solution initially containing 2.5×10^{-2} M $Fe(CO)_4(\eta^2\text{-HFB})$ and the indicated $[PR_3]$. [b] Errors are one standard deviation determined from least-squares fits of the integrated intensity for 30 points covering ~90% reaction. [c] Values in brackets calculated from $\Delta H^* = 88.2$ kJ mol^{-1} and $\Delta S^* = 69.56$ J mol^{-1} K^{-1}.

As already noted, the new data for $Os(CO)_5$ are in good agreement with the earlier study,[15] but the extended temperature range gives revised ΔH^* and ΔS^* values that are higher by 6 kJ mol^{-1} and 22 J mol^{-1} K^{-1}, respectively. The ΔS^* now is distinctly positive as expected for a dissociative mechanism, but is still 44 J mol^{-1} K^{-1} lower than that for $Ru(CO)_5$. For the dissociation of methylacrylate from the $M(CO)_4(\eta^2\text{-methylacrylate})$ systems[16] and of CO from $M(CO)_4(\eta^2\text{-HFB})$, discussed below, the ΔS^* is 12 and 24 J mol^{-1} K^{-1} smaller for Os than Ru, and this may be a general feature of dissociation from these $M(CO)_4L$ systems.

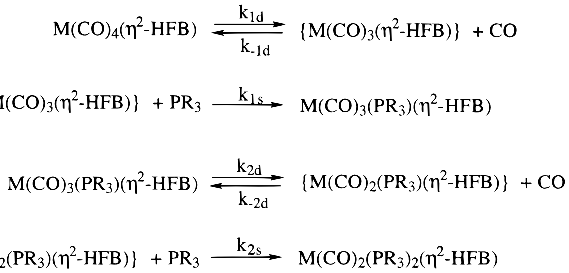
It is qualitatively apparent that the alkyne HFB has a dramatic effect on the CO lability. Substitution on $Fe(CO)_4(HFB)$ was measured at −30 to −40 °C while substitution on $Fe(CO)_5$ is

Table 6. Comparison of Reactivity of $M(CO)_5$ and $M(CO)_4(L)$ Systems with PPh_3

metal species	k_1, s^{-1} 25 °C	ΔH^*,[a] kJ mol^{-1}	ΔS^*,[a] J mol^{-1} K^{-1}
$Fe(CO)_4(\eta^2\text{-HFB})$[b]	9.5	88 ± 2.3	70 ± 10
$Fe(CO)_5$[c]	$\sim 3 \times 10^{-13}$	(167)	(75)
$Fe(CO)_4PPh_3$[d]	5.4×10^{-15}	176 ± 4.7	73 ± 11
$Ru(CO)_4(\eta^2\text{-HFB})$[b]	1.25×10^{-2}	104 ± 2.4	66 ± 8.6
$Ru(CO)_5$[e]	7.0×10^{-5}	$114._5 \pm 3.9$	60 ± 12
$Ru(CO)_4PPh_3$[f]	3.2×10^{-6}	126 ± 1.4	72 ± 4.4
$Os(CO)_4(\eta^2\text{-HFB})$[b]	3.5×10^{-3}	$99._5 \pm 0.8$	42 ± 2.7
$Os(CO)_5$[b,g]	3.3×10^{-10}	133 ± 2.6	21 ± 7.0
$Os(CO)_4PPh_3$[b,g]	1.3×10^{-12}	168 ± 2.9	92 ± 7.5

[a] Values determined from least-squares analysis of published data; errors are one standard deviation. [b] This work, in dichloromethane unless otherwise indicated. [c] Estimated in ref 19. [d] Siefert, E. E.; Angelici, R. J. *J. Organomet. Chem.* **1967**, *8*, 374, in Decalin. [e] Huq, R.; Poë, A. J.; Chawla, S. *Inorg. Chim. Acta* **1980**, *38*, 121, in cyclohexane. [f] Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1975**, 1876, in heptane. [g] In Decalin.

Scheme 2



$$M(CO)_4(\eta^2\text{-HFB}) \underset{k_{-1d}}{\overset{k_{1d}}{\rightleftharpoons}} \{M(CO)_3(\eta^2\text{-HFB})\} + CO$$

$$\{M(CO)_3(\eta^2\text{-HFB})\} + PR_3 \xrightarrow{k_{1s}} M(CO)_3(PR_3)(\eta^2\text{-HFB})$$

$$M(CO)_3(PR_3)(\eta^2\text{-HFB}) \underset{k_{-2d}}{\overset{k_{2d}}{\rightleftharpoons}} \{M(CO)_2(PR_3)(\eta^2\text{-HFB})\} + CO$$

$$\{M(CO)_2(PR_3)(\eta^2\text{-HFB})\} + PR_3 \xrightarrow{k_{2s}} M(CO)_2(PR_3)_2(\eta^2\text{-HFB})$$

too slow to measure at accessible temperatures; $Fe(CO)_4PPh_3$ was studied at 160 to 180 °C. Similarly but less dramatically, the $Os(CO)_4(\eta^2\text{-HFB})$ system was studied in the 10 °C range, while $Os(CO)_5$ was studied from 76 to 115 °C.

The rate constants and activation parameters for PPh_3 substitution on $M(CO)_5$, $M(CO)_4PPh_3$, and $M(CO)_4(\eta^2\text{-HFB})$ systems are summarized in Table 6. A comparison of the rate constants at 25 °C for $M(CO)_5$ and $M(CO)_4(\eta^2\text{-HFB})$ shows that the latter is more reactive by factors of $\sim 3 \times 10^{13}$, 1.8×10^2, and 1×10^7 for M = Fe, Ru, and Os, respectively. The rate acceleration for iron is spectacular. The effect of the HFB resides largely in a lowering of the ΔH^* by ~80, 12, and 33 kJ mol^{-1} relative to $M(CO)_5$, with the interesting result that, while $Fe(CO)_5$ is the least reactive pentacarbonyl, $Fe(CO)_4(\eta^2\text{-HFB})$ is the most reactive alkyne tetracarbonyl derivative.

Increased reactivity due to changing the ligands or the metal may be attributed to either or both of ground-state destabilization or transition-state stabilization. Specifically, the alkyne might destabilize the $M(CO)_4(\eta^2\text{-alkyne})$ complex relative to $M(CO)_5$ by 4-electron repulsion between the filled metal d orbitals and the alkyne $\pi_\perp$ orbital.[19] But the alkyne might stabilize the $\{M(CO)_3(\text{alkyne})\}$ transition state relative to $\{M(CO)_4\}$ to make the alkyne complex more reactive. This is akin to the well-documented cis-effect in $Mn(CO)_5X$ systems, where the theoretical analysis of Lichtenberger and Brown[10a] suggests that stabilization of the intermediate by π-donor ligands is important for cis-labilization. Darensbourg and co-workers[11] have observed examples of the cis-effect for $\eta^1\text{-}O_2CCH_3$,[11a] F,[11b] and 1,2-substituted benzene ligands.[11c] Ideas concerning π-stabilization of unsaturation and filled-filled repulsions have been reviewed and greatly expanded recently by Caulton.[20]

Ground-state effects are easiest to deal with because spectroscopic and structural information are available. In the gas phase, $Ru(CO)_5$ and $Os(CO)_5$[21a,b] have essentially identical geometries, and M−C and C−O bond lengths, so that there is nothing in the ground state to indicate why ΔH^* is 20 kJ mol^{-1} smaller for substitution on $Ru(CO)_5$. In $Fe(CO)_5$,[21c] the M−C bond is ~0.15 Å shorter (compared to ~0.1 Å expected from covalent radii), and the C−O bond is ~0.02 Å longer than in the Ru and Os analogues. These differences are consistent with stronger π-back-bonding in $Fe(CO)_5$, and may account, at least in part, for the estimated 35−50 kJ mol^{-1} higher ΔH^* for $Fe(CO)_5$.

Two theoretical studies have given CO dissociation energies for $Fe(CO)_5$, $Ru(CO)_5$, and $Os(CO)_5$ of 191, 138, and 145 kJ mol^{-1},[22] or 194, 129, and 177 kJ mol^{-1}.[23] The Fe system is complicated by the fact that the lowest energy form of $\{Fe(CO)_4\}$ is a triplet,[24] calculated[22, 23] to be ~7.5 kJ mol^{-1} below the singlet, but CO dissociation is assumed to proceed by the spin-allowed path to the singlet. Pulsed laser pyrolysis[25] has given a first bond dissociation energy of 172 kJ mol^{-1} for $Fe(CO)_5$ in modest agreement with the calculations. More recent calculations[26] give lower values of 156, 101, and 120 kJ mol^{-1} for $Fe(CO)_5$, $Ru(CO)_5$, and $Os(CO)_5$, respectively. For $Ru(CO)_5$ and $Os(CO)_5$, these calculated gas-phase dissociation energies are ~15 kJ mol^{-1} lower than our solution phase ΔH^* values, but the predicted difference in ΔH^* of 19 kJ mol^{-1} is in excellent agreement with the 19 kJ mol^{-1} found here. If one simply relies on the calculated energy differences, then $Fe(CO)_5$ is predicted to have $\Delta H^* \approx 170$ kJ mol^{-1}, consistent with the 167 kJ mol^{-1} estimated by Basolo and co-workers.[15]

It should be noted that the ΔS^* is always more positive for the Ru than for the Os systems (see Tables 1 and 4), and this makes ΔG^* more favorable for $Ru(CO)_5$ by ~10 kJ mol^{-1} at 25 °C. This may reflect some difference in transition state structure as suggested originally by Basolo and co-workers.[15] Indeed, the latest calculations[26] indicate an earlier transition state with a significantly shorter M−C bond for Os than for Ru.

The ground-state structures of $Os(CO)_4(\eta^2\text{-HFB})$ and $Ru(CO)_4(\eta^2\text{-HFB})$ are very similar.[19] The alkyne C−C bond length is 1.276 Å and the $-CF_3$ is bent back 38° from the C−C axis in both. These features show the normal trend from C≡C toward C═C bonding for η^2-alkyne coordination. The M−CO bond lengths are the same, within 0.01 Å of those in the parent $M(CO)_5$ compounds, so that there is no indication that the alkyne has any special effect on the M-CO bonding that would explain the high reactivity of the alkyne derivatives relative to the pentacarbonyls of Ru and Os.

The structure of $Fe(CO)_4(\eta^2\text{-HFB})$ has yet to be determined, but all the spectroscopic information indicates that it has the same ligand arrangement as the other two. The infrared spectra in the CO stretching region (in pentane) are similar with peaks at 2124, 2058, and 2032 cm^{-1} (Fe), 2143, 2073, and 2042 cm^{-1} (Ru), and 2149, 2069, 2061, and 2029 cm^{-1} (Os).

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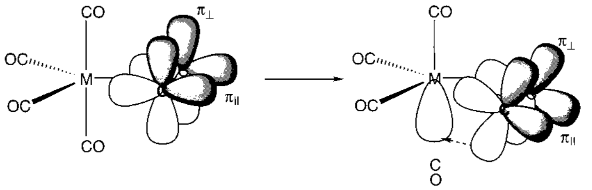

Figure 4. Possible stabilization of the incipient dissociative intermediate by π-electron donation from an alkyne ligand.

The simplest explanation of the labilizing effect of the alkyne seems to be in terms of transition state stabilization.[19] This can occur through π-electron donation from the C≡C system into the vacant site in the dissociative intermediate as illustrated in Figure 4.

In effect, the alkyne acts as a 4-electron donor ligand in the transition state, while π-back-bonding to the alkyne may be largely retained. There is some indication of 4-electron donation by an alkyne from the structure of the coordinatively unsaturated $Os(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2$ complex that has a roughly square pyramidal ligand arrangement with the C−C bond lengthened to 1.32 Å, and a back bending angle of 46°.[27] The latter parameters show a greater tendency to C═C bonding than in the saturated $M(CO)_4(\eta^2\text{-HFB})$ systems described above. In a similar system, Caulton and co-workers[28] have suggested that 4-electron donation by PhC≡CPh may account for the ease of phosphine dissociation from $Ru(\eta^2\text{-}C_2Ph_2)(CO)_2(P^tBu_2Me)_2$. The theoretical work[26] on $M(CO)_4(\eta^2\text{-}C_2H_2)$ systems indicates that the acetylene moves in the transition state as indicated in Figure 4 to a position with an angle of ∼120° to the remaining apical CO, and the C−C bond lengthens to 1.32 Å.[29]

The question remains why this transition state stabilization seems to be in the order Fe ≫ Os > Ru. It is expected that the extent of stabilization should be related to the energy difference between the filled alkyne $\pi_\perp$ orbital and the vacated metal d_σ orbital in the transition state. A qualitative explanation for the greater substitution lability of $Fe(CO)_4(\eta^2\text{-HFB})$ may lie with the lower energy of the 3d orbitals and the well-known tendency of first-row transition-metal complexes to favor 18-electron configurations compared to the second- and third-row metal complexes. Nevertheless, the huge magnitude of the acceleration for $Fe(CO)_4(\eta^2\text{-HFB})$ and the more modest effect for $Ru(CO)_4(\eta^2\text{-HFB})$ seem to require further explanation. The ongoing calculations[26] predict the correct relative reactivity order of Fe > Os > Ru for the $M(CO)_4(\eta^2\text{-}C_2H_2)$ systems, but a detailed rationalization would be premature at this time.

The factors affecting k_2 (i.e., k_{2d}) also are difficult to assess, probably because of compensating effects. Replacement of CO by PR_3 might increase k_{2d} due to the greater steric bulk of the spectator phosphine, but M−C back-bonding might increase because PR_3 is a poorer π-acid and better σ-donor than CO, and this should decrease k_{2d}. It must be noted that there is no compelling evidence for the latter effect from the structures of $Fe(CO)_3(PR_3)_2$ and $Fe(CO)_4(PR_3)$ complexes.[30] Since phosphines are better σ-donors than CO, they might be expected to reduce the stabilizing effect of π-donation from the alkyne in the transition state. But steric interactions between phosphine and alkyne might be relieved in the transition state as the alkyne moves to donate π-electrons to the site trans to the phosphine that has been vacated by the leaving group.

The k_2 results are summarized in Table 1. It is noteworthy that the k_2 values vary from ∼3 times smaller to ∼4 times larger than k_1. Thus replacement of CO by phosphine may either reduce or increase the dissociation rate of the second CO. It appears that basicity of the phosphine, as measured by the pK_a or δ values in Table 1, is not a major factor because the most acidic ($P(OPh)_3$) and most basic (PCy_3) phosphines have k_2 values too large to determine. There is a tendency for a larger cone angle to give a larger k_2, but PEt_3 and especially $P(OMe)_3$ and $P(OPh)_3$ are more reactive than expected on this basis. However, there is some uncertainty about the cone angles,[31] especially for PEt_3 and $P(OMe)_3$, and a judicious choice of values could remove some of this discrepancy. There is a reasonable correlation of k_2 with the steric repulsion parameter E'_R of Choi and Brown,[32] as can be seen by inspection of Table 1, where the data are presented in the order of the E'_R values. There appears to be a steric plateau for $E'_R < \sim 40$ kcal mol^{-1}. The data for $E'_R \geq 39$ give a correlation coefficient of 0.98 for log (k_2) versus E'_R and correctly predicts that PCy_3 and $P(OPh)_3$ should give much higher reactivity than any of the other phosphines studied. Although one might expect a similar correlation with E_R,[33] the $P(OPh)_3$, $P(OMe)_3$, and PEt_3 systems do not correlate well.

The most closely analogous studies for k_2 are those of Chen and Poë[34] on $Ru(CO)_4L$ systems; some of these results are given in Table 4. The reactivity changes were attributed primarily to steric effects. It is notable that, in the above study, all the P donors give a lower reactivity than the $Ru(CO)_5$ parent complex, but k_2 is larger than k_1 for some of the $Os(CO)_3(L)(\eta^2\text{-HFB})$ systems. This could reflect the combined steric effects of the PR_3 and HFB ligands.

Conclusions

The potential for alkyne ligands to act as 2-electron or 4-electron donors enables them to support a variety of structural motifs and to undergo diverse reactions. Previous work from our laboratories[12] and the present study clearly demonstrate a new facet of alkyne ligands, their ability to greatly enhance the rate of CO substitution in d^8 $M(CO)_4(\eta^2\text{-HFB})$ (M = Fe, Ru, Os) complexes. The increased lability is not unexpected in view of the possibile π-donor ability of 2-electron donor alkynes, but the magnitude of the effect is truly remarkable, especially in the case of $Fe(CO)_4(\eta^2\text{-HFB})$. If, as we argue, the enhanced substitution lability is due to stabilization of the dissociative

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(29) A reviewer suggested that the electron-withdrawing ability of hexafluorobutyne might promote lability, given the fomal M(II) oxidation state in the metallacyclopropene extreme of the M−(HFB) interaction (ref 19). The high CO stretching frequencies in $M(CO)_4(\eta^2\text{-HFB})$ were sited as supporting evidence for oxidative addition that would give less M−CO back-bonding. In response, we note that Haszeldine and co-workers (*J. Chem. Soc. A* **1970**, 1964) characterized several analogues of this proposal, namely, derivatives of $(OC)_4Fe(II)$ with fluorinated ligands such as the ferracyclopentane, $Fe(CO)_4(\eta^1,\eta^1\text{-}(CF_2)_4)$, and $Fe(CO)_4(\eta^2\text{-}(C_2F_4))$ which contains the ferracyclopropane extreme of iron−olefin bonding. The former compound has somewhat higher CO stretching frequencies (2150, 2092, 2072, 2056 cm^{-1}) than $Fe(CO)_4(\eta^2\text{-HFB})$, but CO substitution by PPh_3 is sluggish even at 80 °C, giving 53% of the monophosphine derivative, but leaving 24% unreacted starting material after 24 h. The latter compound also does not exhibit CO lability. These observations further emphasize the special labilizing effect of the alkyne in $M(CO)_4(\eta^2\text{-alkyne})$ compounds, especially in comparison with alkene-type ligands.

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16-electron intermediate by π-donation from the $\pi_\perp$ orbital of the alkyne, then the nature of the alkyne should affect the rate of CO substitution. This issue will be addressed in a future publication on the reactions of $Os(CO)_4(\eta^2\text{-HCCH})$ with various phosphines.

Experimental Section

Materials. The hexafluorobut-2-yne (HFB) derivatives $Os(CO)_4(\eta^2\text{-HFB})$ and $Ru(CO)_4(\eta^2\text{-HFB})$ were prepared as described previously,[12] as was $Os(CO)_5$.[35] The phosphines were used as obtained from Aldrich and were stored and handled under a nitrogen atmosphere. Solvents were purified by distillation from appropriate drying agents: sodium benzophenone ketyl for toluene and tetrahydrofuran; phosphorus pentoxide or CaH_2 for dichloromethane; sodium metal for Decalin. The NMR spectra were recorded in dry, deoxygenated CD_2Cl_2 unless otherwise indicated.

The synthesis and characterization of $Fe(CO)_4(\eta^2\text{-HFB})$[18] and some iron,[18] and ruthenium and osmium[13] products, such as $M(CO)_3(PR_3)(\eta^2\text{-HFB})$ and $M(CO)_2(PR_3)_2(\eta^2\text{-HFB})$ (M = Fe, Ru, Os; R = Me, Ph), will be reported in detail elsewhere.

Kinetic Measurements. Stock solutions of $Os(CO)_4(\eta^2\text{-HFB})$ or $Ru(CO)_4(\eta^2\text{-HFB})$ were prepared in the required solvent under nitrogen in serum-capped vials. An appropriate volume (2−5 mL) of the stock solution was transferred by syringe to a vial inside a container in a nitrogen atmosphere in a bath slightly below the ultimate reaction temperature. Solid phosphine was added to the vial before the alkyne complex; liquid phosphine was added by syringe to the solution of alkyne complex. A portion of the mixed solution was transferred by syringe to the infrared cell and this was placed in the thermostating system and the spectrum of the sample was recorded at appropriate intervals. Before each run the cell was brought to temperature in the spectrometer and a solvent blank was recorded.

The thermostating system consisted of a liquid circulating bath filled with 2-propanol (Haake Q bath) or silicone oil (Lauda K6 bath for temperatures > 30°). Liquid circulated from the bath through a double-walled container with an inside diameter just large enough to accommodate the infrared cell. The temperature of the cell was continuously monitored by a Doric copper−constantan digital thermometer that had been calibrated against a Hewlett-Packard Pt resistance thermometer. The temperature typically was constant to ±0.1 °C. The infrared cell (Graseby Specac) was a gastight model with CaF_2 windows and amalgamated foil spacer and gaskets and a stainless steel body.

The infrared spectrometer was a Bomem MB 100 controlled by the software package Spectra-Calc running on an IBM-386 type computer. Special software was developed to control the timing and display the spectra during the kinetic run. Each spectrum was normalized to the absorbance of the initial spectrum in a spectral region where reactants and products did not absorb. The data file from each run was converted to a "text" format so that it could be further analyzed by least-squares methods to determine the rate constants. This analysis was done on an IBM-486 type computer using a least-squares program based on the Marquardt algorithm and written in BASIC.

The NMR samples for $Fe(CO)_4(\eta^2\text{-HFB})$ study were prepared by adding 225 μL of 0.050 M $Fe(CO)_4(\eta^2\text{-HFB})$ in CD_2Cl_2 and 225 μL of phosphine in CD_2Cl_2, both at −78 °C under N_2, to a thick-walled NMR tube also at −78 °C. The contents of the NMR tube was subjected to three freeze−pump−thaw cycles, and then the tube was flame sealed and kept at −78 °C until the spectometer probe was equilibrated at the required temperature. The ^{19}F NMR spectra were run on a Bruker WH-200 instrument and externally referenced to $CFCl_3$. The temperature was monitored by an external Sensotek BAT-10 copper−constantan thermocouple immersed in toluene in a 5-mm OD NMR tube. The probe temperature was steady for 10 min before the sample was introduced. The temperature after the run was measured and the recorded temperature is the average of the beginning and final temperatures. In general, the temperature drift was <0.1 °C. The integrated intensities were obtained from standard routines, using absolute intensities and a common set of processing parameters for each series of experiments. The time dependence of the intensity was fitted to a first-order rate law with the same least-squares program used to fit the infrared data.

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Supporting Information Available: Infrared spectra of products and full kinetic results (4 pages). See any current masthead page for ordering and Web access instructions.

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