uranyl compounds is considered to be small but is being studied in a continuing investigation.

The compounds used in this work were prepared via the same procedures used for the tetrahydrofuran adduct. They were crystalline compounds which were purified by sublimation and afforded H NMR spectra and elemental analyses indicative of the monobasic adducts.

Registry No. 1, 69244-67-3; $UO_2[(CF_3CO)_2CH]_2 \cdot MeOH$, 69244-68-4; $UO_2[(CF_3CO)_2CH]_2 \cdot Me_2SO$, 75172-91-7; $UO_2[(CF_3CO)_2CH]_2 \cdot TMP$, 64708-00-5; $UO_2[(CF_3CO)_2CH]_2 \cdot pyNO$, 34011-51-3; $UO_2[(CF_3CO)_2CH]_2 \cdot Et_3PO$, 75172-92-8; $UO_2[(CF_3CO)_2CH]_2 \cdot HMPA$, 75172-93-9.

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Carbonyl Monoolefin Derivatives of the Group 6 Transition Metals. 2.[1] Kinetics of Olefin Displacement

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The monoolefin complexes *cis*-$M(CO)_4L$(olefin) (M = Cr, Mo, W; L = PR_3) react with triisopropyl phosphite to form *cis*-$M(CO)_4L[P(O(i\text{-}Pr))_3]$ derivatives. The reactions are first order in substrate and zero order in entering ligand with the rates increasing with changes in the metal W ≪ Mo ≪ Cr, changes in the coligand L $PEt_3 < P(i\text{-}Pr)Ph_2 < P(i\text{-}Pr)_2Ph < PPh_3 < P(i\text{-}Pr)_3$, and changes in the olefinic ligand maleic anhydride ≪ dimethyl fumarate < bis(trimethylsilyl) fumarate < dimethyl maleate < ethylene. A dissociative mechanism is proposed involving the rupture of the metal–olefin bond as the rate-determining step.

Introduction

During the last decade homogeneous catalysis has become a field of intense interest to both organic and organometallic chemists. Many important reactions involving olefins, e.g., isomerization, double-bond migration, hydrogenation, and hydroformylation, are efficiently catalyzed by organic derivatives of the heavier group 8 transition metals ruthenium through platinum.[2] In view of the limited availability of these elements it would be desirable to design catalysts based on the more abundant earlier transition metals such as molybdenum or tungsten.

All transition-metal-catalyzed olefin reactions involve the formation and rupture of a metal–olefin bond at some stage of the catalytic cycle. It is, therefore, of prime importance to know how the lability of the metal–olefin bond in transition-metal complexes $ML_mL'_n$(olefin) depends on the nature of the metal and the coligands L and L′ as well as on the substituents at the double bond. As a first step we have investigated the kinetics of olefin displacement in compounds of the type *cis*-$M(CO)_4L$(olefin), where M = Cr, Mo, or W, L = tertiary phosphine, and olefin = maleic anhydride (ma), dimethyl maleate (dmm), dimethyl fumarate (dmf), and bis(trimethylsilyl) fumarate (btf). Although a number of monoolefin derivatives of the group 6 metals are known to date,[3] their reactivity has not yet been investigated in detail.

Table I. Rate Constants for the Reaction $M(CO)_4L$(olefin) + $P(O(i\text{-}Pr))_3 \rightarrow M(CO)_4L[P(O(i\text{-}Pr))_3]$ + Olefin in Dichloroethane Solution at 25 °C

M	L	olefin[a]	$[P(O(i\text{-}Pr))_3]$, M	10^4k, s^{-1}
Cr	PEt_3	ma	0.20	53
Mo	PEt_3	ma	0.10	0.26
			0.20	0.25
	$Pi\text{-}Pr_3$	ma	0.10	80
W	$Pi\text{-}Pr_3$	ma	0.33	<0.1
	PEt_3	dmf	0.40	0.24
	$Pi\text{-}Pr_3$	dmf	0.20	55
			0.33	55
			1.24	52
	$Pi\text{-}Pr_2Ph$	dmf	0.33	13
			0.66	14
	$Pi\text{-}PrPh_2$	dmf	0.19	3.5
			0.33	3.7
	PPh_3	dmf	0.20	31
			1.00	31
	$Pi\text{-}Pr_3$	btf	1.00	120
	$Pi\text{-}Pr_3$	dmm	0.40	1700

[a] ma = maleic anhydride, dmf = dimethyl fumarate, btf = bis(trimethylsilyl) fumarate, dmm = dimethyl maleate.

Experimental Section

Materials. 1,2-Dichloroethane was dried over P_4O_{10} and distilled under nitrogen. Triisopropyl phosphite was distilled at reduced pressure prior to use. The olefin derivatives of chromium, molybdenum, and tungsten were prepared as described previously.[1]

Kinetic Measurements. All reactions with rate constants exceeding 10^{-3} s^{-1} (i.e., $t_{1/2} < 10$ min) were followed by using stopped-flow techniques. Freshly prepared solutions of both reactants in 1,2-dichloroethane were injected via a mixing chamber into a CaF_2 IR cell. The cell was mounted in a close-fitting steel block kept at 25 °C by means of a closed-cycle water thermostat. Optical path lengths of 0.1 or 1.0 mm were employed depending on the concentration of the starting material. A matched cell containing the pure solvent was placed in the reference beam of the spectrometer (Perkin-Elmer 283). Reactions were monitored by following the decrease of absorption of the starting olefin complex at the high-energy carbonyl peak at ~2050 cm^{-1} with the instrument operating in time drive mode. Spectra of the solutions were run after 10 half-lives; complete conversion to the expected cis tetracarbonyl phosphine phosphite complex was observed in all cases.

The slower reactions were carried out in the conventional way in Schlenk tubes under nitrogen. The tubes were wrapped in aluminum foil and stored in a thermostated water bath. Samples were withdrawn

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Table II. Rate Constants for the Reaction $W(CO)_4(PEt_3)(dmf) + P(O(i\text{-}Pr))_3 \rightarrow W(CO)_4(PEt_3)[P(O(i\text{-}Pr))_3]$ + dmf in Dichloroethane Solution[a]

temp, °C	10^4k, s^{-1}
24.7	0.24
34.8	1.10
45.4	4.53

[a] $[P(O(i\text{-}Pr))_3] = 0.5$ M.

at regular intervals, and their IR spectra between 2100 and 2000 cm^{-1} were recorded. The instrument was set at maximum slit width for improved signal/noise ratio. Starting complex and product bands were well separated in all cases.

The olefin complex/phosphite ratio was always kept higher than 15 to ensure pseudo-first-order conditions. Rate constants were calculated by the standard least-squares treatment of plots of ln $(A_t - A_\infty)$ vs. time, which were linear for at least 2 half-lives. Each entry in Table I is the average of at least two individual runs which agreed to better than ±5%.

Results

The rate constants for olefin substitution in cis tetracarbonyl phosphine olefin complexes of chromium, molybdenum, and tungsten are collected in Table I. Attempts were made to include ethylene derivatives in this study. Half-lives of less than 1 s at 25 °C were found, making accurate absorbance readings impossible. Virtually no reaction took place between the maleic anhydride/triethylphosphine derivative of tungsten and triisopropyl phosphite at 25 °C, even over periods of several days. The triisopropylphosphine analogue exhibited some reactivity, enabling us to set an upper limit for k_1 of this compound. At 50 °C slow disappearence of olefin complex occurred in both cases; however, IR spectra of the solutions indicated that other products besides the expected cis phosphine phosphite complexes had been formed.

The reactivity of *cis*-$W(CO)_4(PEt_3)(dmf)$ was suitable for a variable-temperature study. The data in Table II yielded the activation parameters $\Delta H^\ddagger = 26 \pm 1$ kcal/mol and $\Delta S^\ddagger = 9 \pm 3$ cal/(mol deg) (at 25 °C).

Discussion

The rates of reaction of the monoolefin complexes with triisopropyl phosphite are entirely independent of the concentration of entering ligand. This together with a positive value of $\Delta S^\ddagger$ provides convincing proof for a first-order mechanism with the dissociation of the metal–olefin bond being the rate-determining step. As opposed to donor–ligand substitution reactions, which usually obey a two-term rate law, $-d[\text{complex}]/dt = (k_1 + k_2[L])[\text{complex}]$,[4] this mechanistic pattern seems to be typical for five- and six-coordinate metal carbonyl/olefin complexes. Analogous behavior has been found for monoolefin derivatives of manganese[5] and iron,[6] and even the substitution of chelating polyolefins proceeds via a preequilibrium step involving initial dissociation of one metal–olefin bond.[7]

The reactivity of the metal–olefin bond is to a large extent determined by the substituents at the double bond. Electron-withdrawing groups lower the π^* levels of the olefinic ligand, thus increasing the extent of metal-to-ligand back-donation. One would, therefore, expect that for a given metal and phosphine the stability of the metal–olefin bond decreases with decreasing carbonyl stretching frequencies of the complex. This is indeed observed (Table III).

Table III. CO Stretching Vibrations[a] and Relative Rates of Olefin Dissociation[b] (dmf = 1) of Complexes $W(CO)_4(P(i\text{-}Pr)_3)$(olefin)

olefin	ν(CO)	rel rate
ma	2060, 1987, 1963, 1940	<0.002
dmf	2050, 1965, 1947, 1936	1
btf	2047, 1961, 1945, 1935	2
dmm	2051, 1950, 1934, 1924	30
C_2H_4	2029, 1933, 1916, 1905	rapid

[a] In hexane. [b] In dichloroethane at 25 °C.

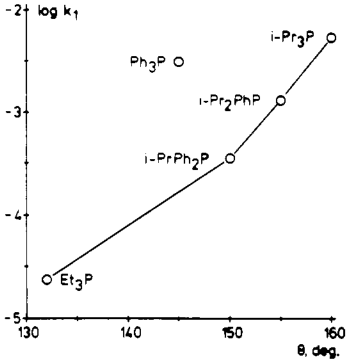

Figure 1. Variation of k_1 of dmf dissociation from $W(CO)_4L(dmf)$ as a function of the cone angle of L.

In view of the large steric influence of the phosphine coligands (vide infra) the small difference between the reactivity of the dmf complex and its btf analogue may be surprising. Molecular models, however, show that, although the bulky Me_3Si groups substantially increase the barrier of rotation of the metal–olefin bond,[1] the complex may actually adopt a conformation in which the remote Me_3Si groups do not interfere with other groups in the molecule. Steric interactions between phosphine and olefin should be roughly the same for the dmm derivative. As opposed to its trans analogue, however, the dmm molecule cannot adopt a conformation with the olefinic double bond and both ester carbonyl groups in the same plane. This reduces the extent of conjugation within the π system of the ligand, rendering dmm a slightly weaker π acid[8] and hence a more labile ligand.

The important role of the metal is demonstrated best by a comparison of the reactivities of the maleic anhydride derivatives. On going from tungsten to molybdenum in $M(CO)_4(P(i\text{-}Pr)_3)$(ma) the rate of olefin dissociation increases by at least 3 orders of magnitude. The step from molybdenum to chromium (in $M(CO)_4(PEt_3)$(ma)) again brings about an increase in k_1 by a factor of 200. This order of reactivity Cr ≫ Mo ≫ W is different from the one usually found for displacement of donor ligands: Mo ≫ Cr > W.[10] The increase of steric strain within the molecule due to the smaller covalent radius of chromium certainly is one important factor contributing to the extreme lability of the chromium–olefin bond.

The phosphine ligands employed in this study span only a small range in terms of electronic properties. Although the donor ability of the coligands is very important for the stability of the metal–olefin bond,[11] we feel that the data presented here

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do not allow any quantitative conclusions.

The dramatic increase of the rate of olefin substitution—more than 2 orders of magnitude—on changing of the coligand from triethylphosphine to triisopropylphosphine points to a pronounced contribution of nonbonding forces to the ground-state free energy of the molecule.

A linear free energy type plot of log k_1 vs. cone angle of the coligand L in the series $W(CO)_4L(dmf)$ is shown in Figure 1. The θ's of the mixed phosphines $P(i\text{-}Pr)_2Ph$ and $P(i\text{-}Pr)Ph_2$ have been taken as the average of the semicone angles of the substituents at phosphorus as suggested by Tolman.[12] This procedure neglects the ligand's ability to rotate about the metal–phosphorus bond until the nonbonding interactions between ligands are minimized. Therefore, the effective cone angles of the mixed phosphines should be a few degrees smaller than indicated in Figure 1, bringing the plot of log k_1 vs. θ even closer to linearity.

The reactivity of the triphenylphosphine derivative is less well understood. From steric considerations alone the rate of dissociation of the tungsten–olefin bond should be smaller by a factor of 10 than what is actually observed. It is equally difficult to invoke electronic properties since the donor ability of the ligands $P(i\text{-}Pr)_nPh_{3-n}$ decreases steadily with decreasing n. There are, however, more examples of anomalous reactivity of group 6 metal carbonyl/triphenylphosphine complexes in both thermal[13] and photochemical[14] reactions. We conclude that the observed kinetics for olefin substitution in $M(CO)_4L$(olefin) derivatives demonstrate the possibility to tune the reactivity of the metal–olefin bond over a wide range by varying the metal M and the coligand L.

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Registry No. $Cr(CO)_4(PEt_3)$(ma), 75248-36-1; $Mo(CO)_4(PEt_3)$(ma), 75266-36-3; $Mo(CO)_4(P(i\text{-}Pr)_3)$(ma), 75248-37-2; $W(CO)_4(P(i\text{-}Pr)_3)$(ma), 75248-38-3; $W(CO)_4(PEt_3)$(dmf), 75248-39-4; $W(CO)_4(P(i\text{-}Pr)_3)$(dmf), 75248-40-7; $W(CO)_4(PPh(i\text{-}Pr)_2)$(dmf), 75266-37-4; $W(CO)_4(PPh_2(i\text{-}Pr))$(dmf), 75248-41-8; $W(CO)_4(PPh_3)$(dmf), 75248-42-9; $W(CO)_4(P(i\text{-}Pr)_3)$(btf), 75248-43-0; $W(CO)_4(P(i\text{-}Pr)_3)$(dmm), 75282-34-7; $P(O(i\text{-}Pr))_3$, 116-17-6; $W(CO)_4(P(i\text{-}Pr)_3)(C_2H_4)$, 75248-44-1.

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Organophosphazenes. 13. Reactions of Hexafluorocyclotriphosphazene with *p*-(Dimethylamino)phenyl Grignard and Lithium Reagents[1]

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The reactions of *p*-(dimethylamino)phenyl Grignard and Lithium reagents with hexafluorocyclotriphosphazene ($P_3N_3F_6$) have been examined. These reactions yield the *p*-(dimethylamino)phenyl-substituted cyclophosphazenes $P_3N_3F_{6-n}[C_6H_4N(CH_3)_2]_n$ (n = 1–3) in moderate to poor yields with the Grignard reagent giving the better yields. The reaction follows a nongeminal pathway, giving an approximately equimolar mixture of cis and trans isomers at the disubstituted stage. In a 6:1 molar reaction of the Grignard reagent with $P_3N_3F_6$, ring degradation appears to be the predominant mode of reaction with the *trans*-2,4,6-$P_3N_3F_3[C_6H_4N(CH_3)_2]_3$ moiety being the only isolable cyclophosphazene. The monosubstituted derivative and the mixture of disubstituted isomers were converted to the geminally substituted mixed-aryl derivatives $P_3N_3F_4C_6H_5[C_6H_4N(CH_3)_2]$ and $P_3N_3F_2(C_6D_5)_2[C_6H_4N(CH_3)_2]_2$ by the Friedel–Crafts reaction. The structures of the new phosphazene derivatives were established by ^{19}F and ^{1}H NMR spectroscopy. A novel dimeric phosphazene, $[P_3N_3F_4C_6H_4N(CH_3)_2]_2$, has also been obtained from the Grignard reaction.

Introduction

The reactions of organometallic reagents with halocyclophosphazenes have proven to be valuable routes to the preparation of organophosphazenes.[2–4] These reactions are often among the most complex in phosphazene chemistry and, depending on the nature of the reactants, can lead to ring substitution or cleavage.[5–7] In substitution reactions both geminal[8–14] and nongeminal[15] reaction pathways have been observed, and the balance between these two routes can be altered by subtle changes in the nature of the reagents employed.[9] In this investigation we have chosen to examine the reactions of hexafluorocyclotriphosphazene ($P_3N_3F_6$) with *p*-(dimethylamino)phenyl Grignard and lithium reagents. A study of this type is of interest in order to examine the effect of the electronic perturbation of the aryl ring (produced by the strongly electron-donating dimethylamino moiety) on the stereochemistry of the substitution reaction.

Experimental Section

Materials and Measurements. Practical grade *p*-bromo-*N*,*N*-dimethylaniline ($p\text{-}BrC_6H_4N(CH_3)_2$) (Eastman) was purified by recrystallizing twice from ethanol. Tetrahydrofuran (THF) was dried

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