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Ligand Displacement Reactions. IV. Catalysis of the Reaction between Trimethyl Phosphite and Tricarbonyl Complexes of Molybdenum and Tungsten

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The reaction between an excess of trimethyl phosphite and the complexes (arene)$M(CO)_3$ (M = Mo, arene = mesitylene; M = W, arene = methyl benzoate) to give *fac*-$[(CH_3O)_3P]_3M(CO)_3$ is markedly catalyzed by trimethyl phosphate, dimethyl sulfoxide, and dimethylformamide but only slightly catalyzed by isopropylamine and tetrahydrofuran. The kinetics fit the rate law: rate = k_2[complex] [phosphite] + k_c[complex] [catalyst]. Values of k_2 and k_c are reported and discussed.

Introduction

Trimethyl phosphite reacts with tricarbonyl(arene)-molybdenum[1] and tungsten[2] complexes according to eq 1, where M = Mo or W. During a study of this

$$(CH_3O)_3P + (\text{arene})M(CO)_3 \longrightarrow fac\text{-}[(CH_3O)_3P]_3M(CO)_3 + \text{arene} \quad (1)$$

reaction, it was found that smaller rate constants were obtained from freshly prepared solutions of trimethyl phosphite than from aged solutions or from solutions of undistilled phosphite. This suggested that the reaction was accelerated by trimethyl phosphate or dimethyl phosphite formed in the trimethyl phosphite by traces of oxygen or moisture.

To assess the importance of any catalysis, a more detailed study was made of the effects of trimethyl phosphate, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), isopropylamine, and tetrahydrofuran (THF). We also obtained comparative data on tricarbonyl(methyl benzoate)tungsten and tricarbonyl(mesitylene)molybdenum and results for reactions of a number of nucelophiles other than trimethyl phosphite. The full data are here presented and discussed.[3]

Experimental Section

Materials.—1,2-Dichloroethane, bp 83–84°, was dried over anhydrous calcium chloride and distilled and stored under a nitrogen atmosphere. Trimethyl phosphate, DMF, methyl cyanide (BDH Ltd.), and triethylphosphine[4] were distilled under nitrogen immediately before use. DMSO (BDH Ltd.) was used without purification.

Preparation of Complexes.—Tricarbonyl(mesitylene)molybdenum and tricarbonyl(methyl benzoate)tungsten were prepared as described previously.[1,2]

Kinetics.—Experimental procedures have been described.[1,2] Accurate rates were obtained from the optical densities of reaction mixtures at *ca.* 325 mμ in 1-cm cells using a Unicam SP 500 spectrophotometer. Products from reactions with triethylphosphine, methyl cyanide, and the cage phosphite $CH_3C(CH_2O)_3P$[5] were identified by their ir spectra.[6]

Results

Spectral Measurements.—Ultraviolet spectra of a solution of tricarbonyl(methyl benzoate)tungsten, trimethyl phosphite, and trimethyl phosphate in 1,2-dichloroethane (Figure 1), recorded at intervals after mixing, showed a clean isosbestic point identical with that obtained with the same concentrations of complex and phosphite, but without phosphate. It is clear that *fac*-tricarbonyltris(trimethyl phosphite)tungsten[2] is the only product. A similar isosbestic point was obtained for the infrared spectra of the reaction mixture, and in an experiment at higher concentrations the product was isolated in good yield and identified by analysis and infrared spectrum.[2] Similar spectra (Figure 1) were recorded when using both DMF and DMSO as catalysts, confirming that in all cases the reactions were clean, and the product was *fac*-$[(CH_3O)_3P]_3M(CO)_3$. The spectra of a mixture of tricarbonyl(methyl benzoate)tungsten and trimethyl phosphate without trimethyl phosphite, however, showed no isosbestic point (Figure 2), probably because the absorption of the product was less than that of the starting material at all wavelengths studied. Trimethyl phosphite was added when the reaction was complete, but there was no change in the spectrum within several hours. An attempt to isolate the complex $[(CH_3O)_3PO]_3W(CO)_3$ yielded only an air-sensitive oil [ν(CO) 1800, 1910 cm^{-1}] which could not be crystallized.

Rate Measurements.—Rates were measured under pseudo-first-order conditions. From the optical densities at time t (D_t) and after 10 half-lives (D_∞), graphs of log ($D_t - D_\infty$) against t were plotted, and pseudo-first-order rate constants k_{obsd} (Table I) for disappearance of tricarbonyl–arene complex were obtained from the slopes. The graphs were linear to beyond 80% reaction. For both tricarbonyl(methyl benzoate)tungsten and tricarbonyl(mesitylene)molybdenum, plots of k_{obsd}[phosphite]$^{-1}$ against [catalyst][phosphite]$^{-1}$ were linear with a common intercept. This suggests the rate expression

$$\text{rate} = k_{obsd}[\text{complex}] = k_2[\text{complex}][\text{phosphite}] + k_c[\text{complex}][\text{catalyst}]$$

The data of Table I were treated by the method of

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[2] A. Pidcock, J. D. Smith, and B. W. Taylor, *ibid.*, *A*, 1604 (1969).

[3] Some of the conclusions have been given briefly: A. Pidcock, J. D. Smith, and B. W. Taylor, *Inorg. Nucl. Chem. Lett.*, **4**, 467 (1968).

[4] K. A. Jenson, P. H. Nielson, and C. T. Pederson, *Acta Chem. Scand.*, **17**, 1115 (1963).

[5] C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 392 (1962).

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TABLE I

FIRST-ORDER RATE CONSTANTS FOR CATALYZED REACTIONS BETWEEN TRIMETHYL PHOSPHITE AND (arene)M$(CO)_3$ IN 1,2-DICHLOROETHANE

Tricarbonyl(methyl benzoate)tungsten (5.7×10^{-5} *M*)

Catalyst	10^3[catalyst], *M*	$10[(CH_3O)_3P]$, *M*	$10^5 k_{obsd}$, sec^{-1}
$(CH_3O)_3PO$	0	2.22	1.80
	2.68	2.22	2.47
	8.03	1.34	2.92
	5.35	2.22	2.95
	8.03	1.64	3.08
	8.03	2.22	3.52
	8.03	1.94	3.66
	8.03	2.53	3.82
	8.03	2.83	4.02
	10.7	2.22	4.08
	13.4	2.22	4.50
DMSO	0	2.37	1.93
	4.53	2.37	12.7
	9.06	2.37	22.6
	13.6	1.58	31.8
	18.1	1.58	43.4
	22.6	1.58	53.2
DMF	0	2.37	1.93
	4.68	2.37	4.51
	9.37	2.37	7.01
	14.1	1.58	8.30
	14.1	2.37	8.85
	18.7	1.58	10.5
	23.4	1.58	12.3

Tricarbonyl(mesitylene)molybdenum (5×10^{-5} *M*)

Catalyst	10^3[catalyst], *M*	$10[(CH_3O)_3P]$, *M*	$10^4 k_{obsd}$, sec^{-1}
$(CH_3O)_3PO$	0	2.04	6.53
	1.44	2.04	6.80
	2.88	2.04	6.95
	4.33	2.04	7.07
	5.77	2.04	7.30
	7.21	2.04	7.55
DMSO	0	2.04	6.53
	1.33	2.04	8.15
	2.65	2.04	9.50
	3.98	2.04	11.1
	5.30	2.04	12.8
	6.63	2.04	14.4
DMF	0	2.04	6.53
	1.62	2.04	7.25
	3.23	2.04	7.98
	4.85	2.04	8.58
	6.46	2.04	9.25
	8.08	2.04	9.72

least squares to find k_2 (corresponding to the uncatalyzed reaction) and the catalytic coefficients k_c (Table II). The constancy of the values of k_2 from measurements with various catalysts and the small standard deviations from measurements over a wide range of catalyst and phosphite concentrations confirm the validity of the above rate expression.

Rate constants (k_{obsd}) for reactions involving the cage phosphite, methyl cyanide, and triethylphosphine are shown in Table III. Second-order rate constants k_2 were calculated from the rate equation[1,2]

$$\text{rate} = k_{obsd}[\text{complex}] = k_2[\text{complex}][\text{phosphite}]$$

Discussion

The Mechanism of the Catalyzed Reaction. (a) **The Rate-Determining Step.**—The rate expression suggests that catalyzed and uncatalyzed reactions occur simultaneously. This is confirmed by the similarity between k_2 obtained here and in previous work[1,2] and by the observation that the second-order rate constant for the reaction between tricarbonyl(methyl benzoate)tungsten and trimethyl phosphate in the absence of phosphite (2.4×10^{-3} M^{-1} sec^{-1}) agrees well with k_c from the catalyzed reaction, $(2.16 \pm 0.12) \times 10^{-3}$ M^{-1} sec^{-1}. The rate-determining steps for uncatalyzed and catalyzed reactions are probably similar and involve S_N2 reactions of phosphite and catalyst with the tricarbonyl(arene)metal complex.[1,2]

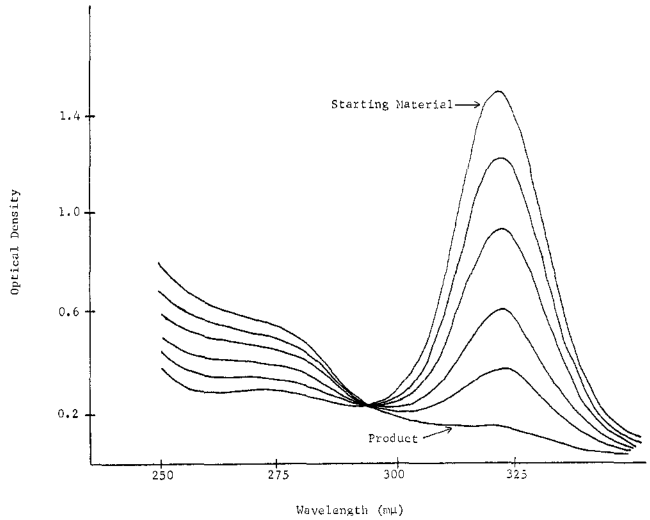


Figure 1.—Isosbestic point for reaction between tricarbonyl(methyl benzoate)tungsten and trimethyl phosphite in the presence of trimethyl phosphate.

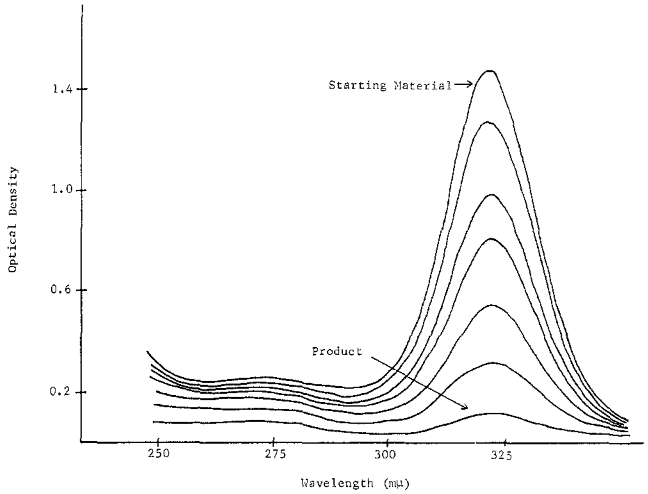


Figure 2.—Spectra for reaction between tricarbonyl(methyl benzoate)tungsten and trimethyl phosphate.

(b) **Steps Following the Rate-Determining Step.**—These cannot be described in detail, but some information is available from the reaction between tricarbonyl(methyl benzoate)tungsten and trimethyl phosphate in the absence of phosphite. The product, which is probably a phosphate complex similar to the known

TABLE II
SECOND-ORDER RATE CONSTANTS AND CATALYTIC COEFFICIENTS FOR THE REACTION BETWEEN (arene)$M(CO)_3$ AND TRIMETHYL PHOSPHITE IN 1,2-DICHLOROETHANE AT 50.0°

Catalyst	10^5k_2, M^{-1} sec^{-1}	10^2k_c, M^{-1} sec^{-1}
Tricarbonyl(mesitylene)molybdenum		
DMSO	319 ± 1	11.8 ± 0.05
DMF	324 ± 3	3.98 ± 0.13
$(CH_3O)_3PO$	321 ± 3	1.33 ± 0.08
None[a]	318 ± 4	. . .
Tricarbonyl(methyl benzoate)tungsten		
DMSO	8.87 ± 2.13	2.29 ± 0.03
DMF	9.56 ± 0.79	0.474 ± 0.009
$(CH_3O)_3PO$	8.31 ± 0.47	0.216 ± 0.012
None[b]	7.74 ± 0.31	. . .
THF		0.0073[c]
$[(CH_3)_2CH]_2NH$		0.0023[c]

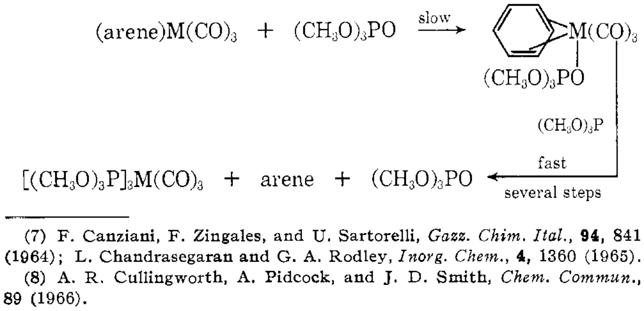
[a] Reference 1. [b] Reference 2. [c] Less precise measurements.

TABLE III
RATE CONSTANTS FOR THE REACTION BETWEEN TRICARBONYL(MESITYLENE)MOLYBDENUM AND VARIOUS LIGANDS (L), IN 1,2-DICHLOROETHANE AT 50.0°

Ligand L	10^2[L], M	10^4k_{obsd}, sec^{-1}	10^3k_2, M^{-1} sec^{-1}
CH_3CN	39.5	28.9	7.30
	29.6	21.5	
	19.8	15.2	
	14.8	10.5	
$CH_3C(CH_2O)_3P$	12.0	10.1	8.47 ± 0.17
	8.16	6.96	
	5.44	4.56	
$(C_2H_5)_3P$			*Ca.* 230[a]
PCl_3			0.69[b]

[a] This value may be in error due to catalysis by oxidation products. [b] Estimated from H. G. S. Woldan and F. Basolo, *J. Amer. Chem. Soc.*, **88**, 2707 (1966).

phosphine oxide[7] complexes, has an absorption spectrum (Figure 2) different from that of the product in the presence of phosphite (Figure 1) but cannot be converted into the tris-phosphite complex by subsequent addition of trimethyl phosphite. This implies that displacement of phosphate from an octahedral complex $[(CH_3O)_3PO]_3W(CO)_3$ is slow, consistent with the observation[8] that exchange between free dimethylphenylphosphine and the complex $[(CH_3)_2(C_6H_5)P]_3Mo(CO)_3$ is not detected by nmr (60 Mc/sec) at 30°. In the catalyzed reaction, the phosphate molecule involved in the rate-determining step must be displaced before a fully substituted complex $L_3M(CO)_3$ is formed, *e.g.*



Attack by the catalyst on the metal atom is considered more likely than attack at a carbonyl carbon atom, since there was no evidence for any CO displacement, which, by analogy with the reactions of $Fe(NO)_2(CO)_2$,[9] would be expected following catalyst attack on a carbonyl carbon atom.

The Effect of Nucleophile.—The ligands studied in the present and previous[10] work may be arranged in order of increasing rate of attack on tricarbonyl(arene) complexes. For $(C_6H_5CO_2CH_3)W(CO)_3$: $((CH_3)_2CH)_2NH < THF < (CH_3O)_3P \ll (CH_3O)_3PO < DMF < DMSO$. For $[C_6H_3(CH_3)_3]Mo(CO_3)$: PCl_3, $C_6H_5PCl_2$[11] $< (CH_3O)_3P < CH_3CN < CH_3C(CH_2O)_3P < (CH_3O)_3PO < DMF < DMSO < (C_2H_5)_3P$. Log k_2(W) for attack on the tungsten complex is approximately proportional to log k_2(Mo) for attack on the molybdenum complex suggesting that similar factors determine the order of reagent reactivity in the two cases. Catalysis is more important for tungsten complexes, which react more slowly than molybdenum complexes.

It has been shown that, for a given donor atom, log k_2 for a substitution reaction at a transition metal is roughly proportional to the basicity or polarizability of the nucleophile, as measured by the difference between its half-neutralization potential and that of diphenylguanidine.[12] For different donor atoms, however, a simple relation between log k_2 and basicity no longer holds. This is confirmed by our results. Thus nitrogen donors react more slowly than phosphorus donors of similar basicity toward protons. The molybdenum and tungsten atoms behave as class b acceptors.[13] Clearly, too, nucleophiles with the X=O group (X = S, C, P) react faster than ethers, and cyanides react faster than amines. Comparisons between rate constants and thermodynamic measurements of basicity are difficult because there are little available data on relative basicities. It is perhaps significant that the order of reactivities of compounds with X=O is the same as the order of their base strengths toward antimony pentachloride[14] and the same as the order of their dipole moments, *e.g.*: DMSO, 4.3 D; DMF, 3.8 D;[15] $(CH_3O)_3PO$, 3.0 D.[16] The kinetic data must, however, reflect the structure of the transition state, which may be such as to favor a particular group of nucleophiles. We suggest that this is the case here: the reactivity of the X=O groups of DMSO, DMF, and $(CH_3O)_3PO$ is probably enhanced by the lack of steric interference from the rest of the molecule. This is consistent with the faster reaction of the cage phosphite $CH_3C(CH_2O)_3P$

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compared with trimethyl phosphite, even though it is a weaker base toward protons.[12]

We have attempted to use the catalytic effect of DMSO in preparative experiments to assist in the displacement of carbon monoxide from tungsten hexacarbonyl by arene, but without success. It is unlikely that other workers have overlooked effects as large as those shown here in kinetic studies on tungsten compounds, even though the phosphorus compounds may not always have been rigorously purified. The catalysis of arene displacements thus at present appears to be unique, although there may be some similarities to the catalysis observed for displacement of CO from $Fe(NO)_2(CO)_2$.[9]

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Proton Magnetic Resonance and Infrared Studies on Bis(*o*-phenylenebisdimethylarsine)cobalt(III) Complexes[1]

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The pmr and infrared spectra from 4000 to 80 K of several bis(diarsine)cobalt(III) complexes are reported. Deduction of structure (whether *cis* or *trans*) has been made on the basis of both types of spectra. Several new *cis* complexes are reported: $[Co(diars)_2(OAc)_2]BF_4$, $[Co(diars)_2CO_3]PF_6$, $[(Co(diars)_2HCO_3)_2HCO_3](BF_4)_3$, $[(Co(diars)_2HCO_3)_2HCO_3](ClO_4)_3$, $[Co(diars)_2(NO_3)_2]ClO_4$, and $[Co(diars)_2ox]PF_6$. Experimental frequency ranges from the literature for the bands in the infrared spectra of these acido groups, bound in various different ways, are tabulated. The nature of the bonding in the acetato, thiocyanato, carbonato, and oxalato groups has been determined by comparison of their infrared spectra with the ranges collected from the literature. The dimeric bicarbonato cation is quite unusual in that the bridging unit appears to be a bicarbonato group.

Introduction

Some years ago Jørgensen[2] proposed that complexes containing both hard and soft bases would be less stable than those containing only hard or only soft bases. Indeed, few complexes have been studied in which a hard acid such as Co(III) is bound to both hard and soft bases. We have prepared and characterized a series of cobalt(III) complexes containing two molecules of the soft base *o*-phenylenebisdimethylarsine (hereafter denoted diarsine (diars)) and various hard bases, either two monodentate anions or one bidentate anion. Nyholm and coworkers have prepared a number of complexes of the type $Co(diars)_2X_2^+$, where X = Cl, Br, I, and NCS[3] and acetate[4] ions, but the structures were determined only for the *cis*- and *trans*-dichloro and -dibromo isomers.[5,6] The series $Co(diars)_2NOX^+$, where X = Cl, Br, I, and NCS, has also been studied,[7] as have the visible and near-infrared spectra of the *trans*-dihalo complexes.[8]

The *cis* and *trans* isomers had been characterized using visible,[5] infrared,[7] and low-frequency infrared spectroscopy,[6] but the definitive assignment was the result of an X-ray study on the *trans*-dichloro complex.[6] We have found that the pmr spectra can clearly, quickly, and easily differentiate between isomers, even if the samples are somewhat impure. After ascertaining the structures of our complexes using pmr, we were able to assign a number of infrared bands and to show how the infrared spectra could be used in determining whether a pure sample of a given bis-diarsine complex was *cis* or *trans*. Further, we were able to determine the nature of the linkages between the diacido groups and the cobalt(III) ion from the infrared spectra.

Experimental Section

Reagents.—Most of the reagents used were reagent grade and were not further purified. The deuterated solvents used in recording the pmr spectra were obtained from the Merck Chemical Co. The *o*-arsanilic acid (one sample from Fluka A. G. Chemische Fabrik, "purum;" one from Schuchardt) was recrystallized. Deionized water and 99% undenatured ethanol were used. Almost all samples used for physical measurements had been washed with ethanol and then ether and dried under high vacuum (using a mercury diffusion pump) for 4 hr and gave good analyses. The complexes, particularly the *cis* isomers, are somewhat light sensitive, and most operations were carried out in blackened containers.

Diarsine.—The ligand *o*-phenylenebisdimethylarsine was prepared from *o*-arsanilic acid as described by Eberly and Smith[9] and Kalb.[10] From 81 g of starting material, 22.7 g of ligand, bp

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(1) Abstracted from a portion of a thesis submitted by B. K. W. Baylis to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the Ph.D. degree, 1968. The laboratory work was done at the Anorganisches-Chemisches Institut of the Technische Hochschule, Munich, West Germany.

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