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TRIMETHYLAMINE *N*-OXIDE PROMOTED REACTIONS OF MANGANESE, MOLYBDENUM AND TUNGSTEN CARBONYL COMPLEXES

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Summary

Substitution reactions of $PhMn(CO)_5$ and η^5-$C_5H_5M(CO)_3X$ complexes (M = Mo or W; X = halide) with phosphines and arsines proceed rapidly at room temperature in the presence of $(CH_3)_3NO$ to give *cis*-$PhMn(CO)_4L$, or *cis*-η^5-$C_5H_5M(CO)_2(L)X$, respectively. Stereoselectivity, product yields, and reaction rates are dramatically enhanced by use of the amine oxide reagent.

Introduction

Trimethylamine *N*-oxide has been shown recently to be a valuable synthetic reagent in the preparation of substituted metal carbonyl complexes. For example, η^4-butadieneiron tricarbonyl [1] and heavily substituted Group VI carbonyls $L_2M(CO)_4$ and $L_3M(CO)_3$ [2] have been prepared under mild conditions by the use of this reagent. Substituted metal carbonyl clusters are similarly available by this route [3,4]; the lower temperatures made possible by the use of the amine oxide avoids declusterification and other undesirable side reactions. Gladysz and coworkers [5] have recently demonstrated the utility of this route for decarbonylation of arylmanganese compounds which were not amenable to thermal or photochemical methods. The mechanism of the promoting effect is not known with certainty, but the isolation of trimethylamine complexes of iron [6] and molybdenum [2] from the reactions of the respective carbonyls, and the demonstration that CO_2 is evolved in the former case suggest nucleophilic attack at carbonyl carbon, loss of CO_2 and (in the absence of donor ligands) complexation by Me_3N. These recent studies prompt us to report at this time the results of studies of the reactions of $PhMn(CO)_5$ and η^5-$C_5H_5M(CO)_3X$ (M = Mo or W; X = halide) with the amine oxide reagent both in the presence and absence of donor ligands.

Experimental

$[CpMo(CO)_3]_2$ and $Mo(CO)_6$ were used as received from Ventron, Inc. $[CpW(CO)_3]_2$ [7], $CpM(CO)_3X$ (X = halide) [8], $CpM(CO)_3CH_3$ [8] and $PhMn(CO)_5$ [9] were synthesized according to literature procedures. Triphenylphosphine and triphenylarsine were recrystallized from ethanol. Trimethylamine *N*-oxide dihydrate was purchased from Aldrich Chemical Co. and dehydrated prior to use by vacuum sublimation. Solvents were dried by standard methods and purged with argon just prior to use. Argon atmospheres were maintained during all operations, including admission of argon to evacuated flasks after rotary evaporation. Infrared and NMR spectra were obtained on Beckman 4240 and Varian EM-390 instruments, respectively. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory.

Synthesis of cis-$PhMn(CO)_4PPh_3$

$PhMn(CO)_5$ (0.275 g, 1.06 mmol) and triphenylphosphine (0.341 g, 1.3 mmol) were dissolved in approximately 40 ml of methylene chloride under argon. Trimethylamine *N*-oxide (0.088 g, 1.17 mmol) was added with vigorous magnetic stirring. After 30 minutes, no starting material remained, as judged by infrared analysis of an aliquot of the reaction mixture. Solvent was removed by rotary evaporation leaving a yellow oil, which was dissolved in 1/1 CH_2Cl_2/hexane and chromatographed on neutral alumina (Activity Grade 1). A single yellow band developed. Removal of solvent followed by recrystallization (acetone/ether) afforded 0.524 g of the yellow crystalline product (88% yield). Analysis: Found C, 66.86, H, 4.06. $C_{28}H_{20}MnO_4P$ calcd.: C, 66.40, H, 3.95%.

Synthesis of cis-$CpMo(CO)_2(PPh_3)I$

$CpMo(CO)_3I$ (0.1193 g, 0.32 mmol) and PPh_3 (0.2040 g, 0.78 mmol) were dissolved in 25 ml CH_2Cl. With argon being bubbled through the magnetically stirred solution, Me_3NO (0.0465 g, 0.62 mmol) was added. The reaction was terminated after 15 minutes and solvent removed by vacuum rotary evaporation. The residue was taken up in $CHCl_3$ and chromatographed as above with 1/1 $CHCl_3$/hexane. A single red-orange band was observed and collected. Removal of solvent (at room temperature) and crystallization from $CHCl_3$/hexane afforded 0.183 g of burnt orange crystals (90% yield). The product was characterized by comparison of its IR and ^1H NMR spectra with literature [10] values. Similarly prepared (yield) were: *cis*-$CpMo(CO)_2(AsPh_3)I$ (80%) $CpMo(CO)_2[PPh_2(o\text{-tolyl})]I$ (67%) and *cis*-$CpW(CO)_2(PPh_3)Cl$ (71%).

Isomerization of $CpMo(CO)_2(PPh_3)I$ by Me_3NO and Me_3N

Isomerization of *cis*-$CpMo(CO)_2(PPh_3)I$ to the thermodynamic isomeric mixture is described in the following section and shown in Fig. 2. An even more rapid rate of isomerization induced by Me_3N was shown by bubbling the latter through CH_2Cl_2 solutions of either *cis*- or *trans*-$CpMo(CO)_2(PPh_3)I$. In both cases isomerization to the thermodynamic [10] (~50/50) isomeric mixture was complete in the time required for sampling. No other molybdenum-containing products were isolated.

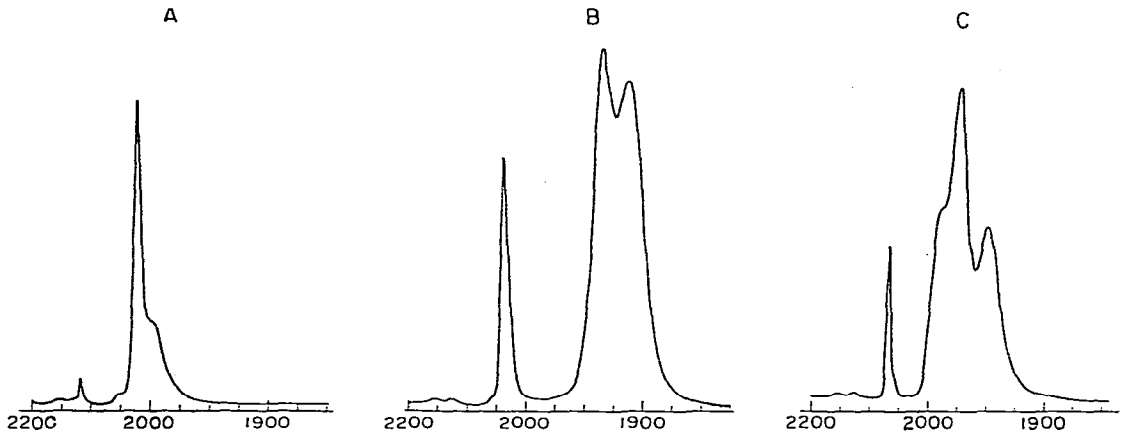

Fig. 1. IR spectral changes accompanying addition of Me_3NO and PPh_3 to $PhMn(CO)_5$ (CH_2Cl_2 solution). A: $PhMn(CO)_5$ in CH_2Cl. B: After addition of Me_3NO. C: After addition of Ph_3P.

Results and discussion

Phenylmanganese pentacarbonyl and triphenylphosphine are reported to react slowly in methylene chloride solution at room temperature [9] to give *cis*-$PhMn(PPh_3)(CO)_4$ (64% yield after three days). In the presence of Me_3NO, this reaction is virtually instantaneous, with isolated yields of the product in excess of 90%. The product was characterized by IR, melting point and elemental analysis. Further investigations strongly suggest that the reaction proceeds as shown in eq. 1 and 2. Thus, when the manganese complex in CH_2Cl_2 solution is treated with Me_3NO in the absence of the phosphorus ligand, the

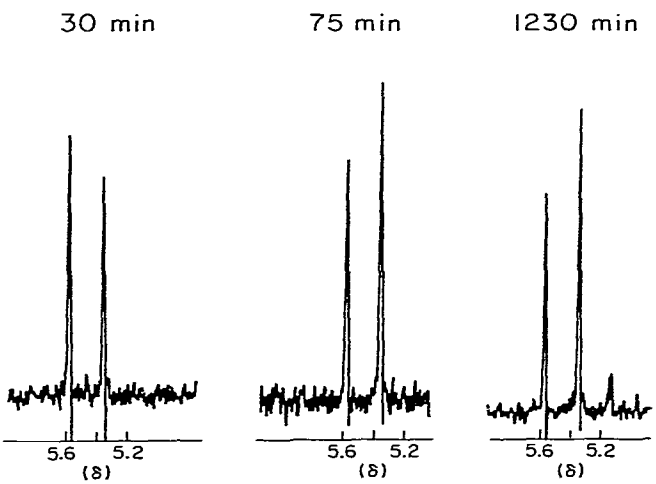

Fig. 2. Proton NMR spectra of the C_5H_5 region of the $CpMo(CO)_3I$, PPh_3, Me_3NO reaction mixture as a function of time. Resonances at δ 5.58, 5.34, and 5.11 ppm are due to $CpMo(CO)_3I$, *cis*-$CpMo(CO)_2(PPh_3)I$ and *trans*-$CpMo(CO)_2(PPh_3)I$, respectively.

colorless solution turns yellow immediately and $PhMn(CO)_5$ $\nu(CO)$ bands at

$$PhMn(CO)_5 + Me_3NO \rightarrow cis\text{-}PhMn[Me_3N](CO)_4 + CO_2 \quad (1)$$

$$cis\text{-}PhMn[Me_3N](CO)_4 + PPh_3 \rightarrow cis\text{-}PhMn(PPh_3)(CO)_4 + Me_3N \quad (2)$$

2115w and 2018vs cm^{-1} are replaced by new absorptions at 2030, 1932, and 1910 cm^{-1} assigned to *cis*-$PhMn(Me_3N)(CO)_4$. Addition of triphenylphosphine to the solution results in rapid ($t < 5$ min) replacement of these absorptions by new bands at 2068, 1990, 1972, and 1952 cm^{-1} readily assignable to *cis*-$PhMn(PPh_3)(CO)_4$ (lit. [9]; 2066, 1992, 1972, 1949 cm^{-1}). These changes are listed in Fig. 1. The high yield and short reaction time required for this reaction demonstrate the utility of the amine oxide for synthetic purposes.

Since only the *cis* isomer of $PhMn(PPh_3)(CO)_4$ is known [9], this reaction gives no information regarding the stereoselectivity of the overall process. The potential of this reagent for stereoselective synthesis is best shown by the data obtained for the sequence shown in eq. 3 ($Cp = \eta^5\text{-}C_5H_5$):

$$CpMo(CO)_3I + PPh_3 + Me_3NO \rightarrow cis\text{-}CpMo(CO)_2(PPh_3)I + Me_3N\uparrow + CO_2 \quad (3)$$

Dissolution of $CpMo(CO)_3I$ and the phosphorus ligand in methylene chloride followed by slow addition of the Me_3NO as a slurry in CH_2Cl_2 leads to complete conversion to the substituted product. The identity of the product was established by comparison of IR and ^1H NMR spectral data to those previously reported [10]. The selective formation of the *cis* isomer was demonstrated by carrying out the reaction in an NMR tube ($CDCl_3$ solvent) which showed only the *cis* isomer up to 60% conversion (~2 h) (Fig. 2). After 18 h, ~10% of the *trans* isomer had formed, due in part to slow thermal *cis* → *trans* isomerization.

Large excesses of Me_3NO must be avoided in these reactions; control experiments show that it promotes isomerization. Byproduct trimethylamine causes *cis* ⇌ *trans* isomerization (Experimental Section) even more rapidly than the amine oxide itself. Maximum isomeric purity of product from the Me_3NO-promoted substitution reaction is obtained by bubbling argon through the reaction mixture. We note that several $CpM(CO)_2(L)I$ complexes are catalytically isomerized by alkyllithium reagents [11]. This suggests a general mechanism for isomerization of these complexes by strong bases, possibly via nucleophilic attack at coordinated carbon monoxide.

The molybdenum and tungsten halide complexes $CpM(CO)_3X$ (X = Cl, Br, or I) gave similar results with a variety of ligands, demonstrating the efficacy of this route for preparing the substituted derivatives. For example, *cis*-$CpMo(CO)_2(AsPh_3)I$ was prepared in 80% yield (CH_2Cl_2 solution room temperature, 4 h). Previous syntheses of this complex involved refluxing a benzene solution of $CpMo(CO)_3I$ and $AsPh_3$ (18 h, 38% yield [12] or photolysis for 30 h, giving a 73% yield [13]). Previous attempts at synthesizing $CpMo(CO)_2(L)I$ complexes containing bulky mixed phenyl, *o*-tolylphosphines via thermal substitution were not successful [14], but use of the amine oxide allowed isolation of $CpMo(CO)_2[P(o\text{-tolyl})Ph_2]I$ in 67% yield (CH_2Cl_2 solution, 25°C, 7 h reaction time). The product was obtained as an 80/20 *cis,trans* mixture. However, NMR spectral of aliquots of the reaction mixture showed that the *cis* isomer was the initially formed product. Isomerization apparently results from the long reac-

tion time required and the presence of Me_3N and an excess of Me_3NO (vide supra).

IR spectra of CH_2Cl_2 solutions of $CpMo(CO)_3I$ and (Me_3NO) in the absence of added nucleophiles gave no evidence for formation of a trimethylamine complex or of $[CpMo(CO)_2I]_2$. Extensive decomposition occurred over a 2—3 hour period at room temperature. Thus, if $CpMo(CO)_2(NMe_3)I$ is formed in these reactions, it decomposes too rapidly for observations. With acetonitrile as solvent, new ν(CO) bands at 1975 and 1885 cm^{-1} indicate formation of $CpMo(CO)_2(CH_3CN)I$. Attempts to isolate this species in pure form have so far met with failure. The samples invariably decomposes during work-up, reforming $CpMo(CO)_3I$ and non-carbonyl-containing products.

Preliminary investigations of the reactions shown in eq. 4 (L = PPh_3, or $P(OP)_3$) further indicate the high stereoselectivity provided by use of the

$$LMo(CO)_5 + L \xrightarrow{Me_3NO} cis\text{-}L_2Mo(CO)_4 \qquad (4)$$

amine oxide route. Since both *cis* and *trans* isomers of $L_2Mo(CO)_4$ are known and are not readily interconverted under the reaction conditions (CH_2Cl_2, 25° C), this strongly suggests that the *cis* isomer is the kinetically controlled product. When these reactions are conducted in the absence of added ligand, infrared spectroscopic evidence indicates the formation of *cis*-$(L)(Me_3N)Mo(CO)_4$. The affinity of the $LMo(CO)_4$ unit for the trimethylamine complicates this system and dictates further study before definitive statements concerning reaction mechanisms and stereochemistry are possible.

The prevalence of *cis* isomers in the cases studied to date might be due to preferential attack of amine oxide at the *cis* carbonyls, followed by elimination of CO_2 from this position. Such a pathway would involve a coordinatively unsaturated intermediate that might undergo intramolecular rearrangement during its lifetime. Cases in which such intermediates rearrange slowly [15,16], as well as others in which rearrangement is rapid [17,18] are known.

We cannot be sure on the basis of these prior studies whether the intermediates generated in the present work undergo rearrangement during their lifetimes. If the intermediate were slow to rearrange, the stereochemistry of the product formed upon binding of L would reflect the location of initial amine oxide attack. On the other hand, if rearrangement is rapid, the site of initial amine oxide attack is not necessarily reflected in the product stereochemistry. The predominantly *cis* geometry of the products is consistent with expectations based on the Site Preference model for *cis* labilization [18c]; that is, the heteroligand is preferentially located in a position *cis* to the vacancy in the intermediate (the basal position of a square pyramid in the case of the five-coordinate intermediate such as $PhMn(CO)_4$ or $LMo(CO)_4$).

While the results obtained thus far do not permit the conclusion that amine oxide attack occurs at the *cis*-CO positions, other lines of evidence do suggest that nucleophilic attack occurs there preferentially [19—21]. Additional studies involving stereospecifically labeled molecules will be required to uncover additional mechanistic details.

It is important to note that product Me_3N can effect rapid isomerization of a kinetically controlled products. Catalysis of isomerization very probably

arises through nucleophilic attack at CO, with consequent labilization of the positions *cis* to the carbonyl [21].

There is a reasonable correlation between reactivity of the metal carbonyl Me_3NO and stretching force constants based on a simple energy-factored force field [22]. As an example $CpMo(CO)_3I$ ν(CO) 2046, 1989, 1968 cm^{-1}; K_1 = 15.70, K_2 = 16.35 [23] reacts readily, while $CpMo(CO)_3CH_3$ (ν(CO) 2018, 1950, 1946 cm^{-1}; K_1 = 15.49, K_2 = 15.80 [23]), is unreactive under the same conditions after several hours. Koelle [2] has suggested a parallel between ν(CO) and severity of reaction conditions in metal carbonyl—amine oxide reactions, and similar correlations exist for nucleophiles such as amines [20] and organolithium compounds [24]. Our results and those of Koelle [2] suggest that the requirement that $K > 16.0$ and/or $\nu(CO) > 2000$ cm^{-1} are useful guidelines for predicting whether the amine oxide reagent will react with a given substrate.

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