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Note

Efficient microwave syntheses of the compounds $Os_3(CO)_{11}L$, L = NCMe, py, PPh_3

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ABSTRACT

The results of simple microwave-assisted ligand substitution reactions of $Os_3(CO)_{12}$ are reported. In a remarkably short period of time, the labile complex $Os_3(CO)_{11}(NCMe)$ is prepared in high yield without the need for a decarbonylation reagent such as trimethylamine oxide. Microwave irradiation of $Os_3(CO)_{12}$ in a relatively small amount of acetonitrile is shown to be a useful first step in two-step, one-pot syntheses of the cluster complexes $Os_3(CO)_{11}(py)$ and $Os_3(CO)_{11}(PPh_3)$.

1. Introduction

Well over 1000 publications describing osmium carbonyl cluster chemistry have appeared in the scientific literature. Despite the fact that dodecacarbonyltriosmium(0), $Os_3(CO)_{12}$, is the most important osmium cluster precursor, its stability inhibits its reactivity [1]. The Os–CO bonds are relatively inert, so that even simple ligand substitution reactions require prolonged periods of heating and often lead to multiple products. For example, refluxing a toluene solution of $Os_3(CO)_{12}$ and excess triphenylphosphine for 14 h results in the formation of three products, $Os_3(CO)_{11}(PPh_3)$, $Os_3(CO)_{10}(PPh_3)_2$ and $Os_3(CO)_9(PPh_3)_3$, in 10%, 29%, and 52% yields, respectively [2].

In order to avoid severe thermal conditions and lack of selectivity, several methods of activating $Os_3(CO)_{12}$ have been developed. Chief among these are the adsorption of $Os_3(CO)_{12}$ on a solid support, the exposure of a solution of $Os_3(CO)_{12}$ to UV radiation, and the substitution of one or more CO ligands with a much more labile group. A number of osmium clusters containing hydride ligands may be synthesized in high yield with the use of silica-supported $Os_3(CO)_{12}$ [3]. Broadband UV photolysis of solutions of $Os_3(CO)_{12}$ at low temperature is quite effective for the preparation of certain substituted clusters such as $Os_3(CO)_{12-n}(PR_3)_n$ [4,5]. More common by far, however, is the use of the labile complexes $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$ as starting materials for osmium cluster synthesis [6,7].

The standard method for the conversion of $Os_3(CO)_{12}$ to $Os_3(CO)_{11}(NCMe)$ involves the drop-wise addition of a solution of freshly sublimed trimethylamine oxide to a suspension of $Os_3(CO)_{12}$ in acetonitrile, followed by a lengthy period of stirring at room temperature [7]. This procedure provides the desired product in up to 80% yield, but it requires the exclusion of air and moisture and takes over 12 h to complete. Another route to the monosubstituted acetonitrile derivative is the UV photolysis of a dry, air-free MeCN solution of $Os_3(CO)_{12}$ at low temperature [5]. Photosubstitution occurs in only 1 h, but the yield is just 70%.

The efficiency of many preparative procedures has been significantly improved through the use of microwave irradiation [8]. Microwave-enhanced organometallic reactions were first reported 20 years ago when Mingos, Baghurst and coworkers carried out the syntheses of $[M(diene)_2Cl]_2$ complexes from $RhCl_3$ and $IrCl_3$, as well as the synthesis of $[Cp_2Rh]PF_6$ from $RhCl_3$, using methanol or ethanol as solvent [9]. In subsequent years, these researchers and others have prepared dozens of metal arene and/or Cp complexes by microwave heating [10–16]. Several microwave-assisted ligand substitution reactions involving group 6 metal carbonyls have also been reported [17–19].

Two recent studies have shown that microwave irradiation allows for fast and efficient transformations of $Os_3(CO)_{12}$. The reaction of $Os_3(CO)_{12}$ with H_2 in a microwave reactor results in the nearly quantitative production of $H_2Os_3(CO)_{10}$ in only 15 min [20], while the high-nuclearity cluster anion $[Os_{10}C(CO)_{24}]^{2-}$ is prepared directly from $Os_3(CO)_{12}$ with microwave heating of a diglyme solution for just over 1 h [21]. We wondered whether substitution of one or more CO ligands with MeCN ligands might be possible in a microwave reactor without the use of Me_3NO as a

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decarbonylation reagent. This note describes the results of our investigations.

2. Experimental

All reactions were carried out in a Discover-S microwave reactor (CEM Corp., Matthews, NC). Thick-walled 35-mL glass reaction vessels with Teflon-lined caps were provided by CEM. Caution must be exercised due to the toxic nature of CO and metal carbonyl compounds. All manipulations must be carried out in a highly efficient fume hood. Extra care must be taken when the reactions are under pressure; the microwave reactor must be placed in the fume hood and the hood sash must be left down until a few minutes after the pressure has been released. A new cap should be used to seal the reaction vessel for each reaction described below. The $Os_3(CO)_{12}$ and triphenylphosphine (PPh_3) were purchased from Strem, while all other reagents were purchased from Aldrich. All chemicals were used as received. Infrared spectra were recorded on an Avatar 320 FT-IR spectrophotometer. ^1H NMR spectra were recorded on an EM360A spectrometer. Preparative thin-layer chromatography (TLC) was carried out in air on Analtech 0.25 mm 60 Å silica gel on glass plates.

2.1. Synthesis of $Os_3(CO)_{11}(NCMe)$

A 75.8 mg (0.0836 mmol) sample of $Os_3(CO)_{12}$ was added to 6 mL of acetonitrile in a 35-mL reaction vessel equipped with a magnetic stir bar. The vessel was capped, placed in the microwave reactor, and irradiated at 200 W with a high rate of stirring. A temperature of 150 °C was maintained for 5 min. The vessel was placed in a water bath at 45 °C and the solvent was evaporated under a stream of N_2 gas leaving a green–yellow residue. The residue was dissolved in CH_2Cl_2, and TLC was performed with an eluent of hexane (65 mL), CH_2Cl_2 (35 mL) and acetonitrile (1 mL) to give 6.2 mg of unreacted $Os_3(CO)_{12}$, $R_f = 0.69$, and 63.4 mg (82.4% yield) of yellow $Os_3(CO)_{11}(NCCH_3)$, $R_f = 0.49$. The IR (CH_2Cl_2) and ^1H NMR ($CDCl_3$) spectra of $Os_3(CO)_{11}(NCMe)$ were identical to those reported previously [6].

2.2. Synthesis of $Os_3(CO)_{11}(py)$

A mixture of $Os_3(CO)_{12}$ (0.0758 g, 0.0836 mmol) and 6 mL acetonitrile was irradiated in the microwave reactor as described above for the synthesis of $Os_3(CO)_{11}(NCMe)$. The solvent was evaporated, and then 10 mL dichloromethane was added along with 0.10 mL (1.2 mmol) pyridine. The vessel was capped and placed back into the microwave reactor where the mixture was stirred at the highest rate and irradiated with an initial power of 100 W. The temperature was kept between 44 and 47 °C for 2 min. The solvent was evaporated, and the products were separated by TLC using a 1.75:1 hexane:CH_2Cl_2 solvent mixture to give two bands with $R_f = 0.71$ and 0.49. The lower band consisted of 53.7 mg (67.1% yield) of yellow–orange $Os_3(CO)_{11}(C_5H_5N)$. The IR (CH_2Cl_2) and ^1H NMR ($CDCl_3$) spectra of $Os_3(CO)_{11}(py)$ were identical to those reported previously [6]. The top band required further separation with an eluent of 3:1 hexane:CH_2Cl_2 and consisted of 3.9 mg of $Os_3(CO)_{12}$ and 6.3 mg of an as-yet unidentified yellow product, IR (ν_{CO}, CH_2Cl_2): 2104(m), 2063(vs), 2052(vs), 2017(vs), 2009(s,sh), 1991(s), 1967(m), 1942(w).

2.3. Synthesis of $Os_3(CO)_{11}(PPh_3)$

This compound was prepared in a manner similar to the two-step, one-pot method described above for the synthesis of $Os_3(CO)_{11}(py)$. In the first step, 74.9 mg (0.0826 mmol) of $Os_3(CO)_{12}$ was used. For the second step, triphenylphosphine (23.5 mg, 0.0896 mmol) was used instead of pyridine, and the mixture was stirred at room temperature (23 °C) for 1 h instead of being subjected to microwave heating. Separation by TLC with an eluent of 1.75:1 hexane:CH_2Cl_2 yielded 4.9 mg of unreacted $Os_3(CO)_{12}$, 75.1 mg (79.7%) of yellow $Os_3(CO)_{11}(PPh_3)$, $R_f = 0.76$, and 12.2 mg (10.7%) of orange $Os_3(CO)_{10}(PPh_3)_2$, $R_f = 0.55$. The IR (CH_2Cl_2) and ^1H NMR ($CDCl_3$) spectra of the products were identical to those previously published [5]. The melting point of $Os_3(CO)_{11}(PPh_3)$ also matched the reported value [22]. Conducting the second step of this synthesis in the microwave reactor at temperatures between 35 and 42 °C resulted in lower yields (~71%) of $Os_3(CO)_{11}(PPh_3)$ and higher yields (~14%) of $Os_3(CO)_{10}(PPh_3)_2$.

3. Results and discussion

Heating a mixture of $Os_3(CO)_{12}$ and acetonitrile at 150 °C for only 5 min in a microwave reactor produces $Os_3(CO)_{11}(NCMe)$ in 82% yield. About 8% of the dodecacarbonyl starting material remains unchanged. The key to the success of this reaction appears to be attaining a temperature above 145 °C. When exposed to microwave radiation, a solvent in a closed system can quickly reach temperatures far above its normal boiling point. There is no reason to invoke special microwave-induced effects to explain the dissociation of carbonyl ligands. We assume that thermal excitation alone is at work since we have found that the replacement of CO ligands with MeCN ligands does not occur at temperatures below 135 °C. Significant degradation of the desired product occurs at temperatures above 190 °C. Attempts to prepare $Os_3(CO)_{10}(NCMe)_2$ by prolonged exposure of the reaction mixture to microwave radiation (up to 20 min) at 150 °C were unsuccessful and led to reduced yields of $Os_3(CO)_{11}(NCMe)$.

In order to determine the efficacy of using the unpurified microwave-irradiated mixture as a first step in the synthesis of other triosmium carbonyl cluster complexes, we removed the excess acetonitrile and reacted the residue with either pyridine or triphenylphosphine in CH_2Cl_2. The compounds $Os_3(CO)_{11}(py)$ and $Os_3(CO)_{11}(PPh_3)$ were produced in 67% and 80% yield, respectively, based on the initial amount of $Os_3(CO)_{12}$ used. The conventional method of preparing $Os_3(CO)_{11}(py)$ involves converting $Os_3(CO)_{12}$ to $Os_3(CO)_{11}(NCMe)$, then reacting $Os_3(CO)_{11}(NCMe)$ with pyridine to give an overall yield of 59% over a period of at least 14 h [7]. Photolysis of a dichloromethane solution of $Os_3(CO)_{12}$ containing excess pyridine gives a 60% yield of $Os_3(CO)_{11}(py)$ in 6 h [23]. One report described the preparation of $Os_3(CO)_{11}(PPh_3)$ in 50% yield directly from $Os_3(CO)_{12}$ in just 10 min with the use of Me_3NO and $Ni(CO)_2(PPh_3)_2$ [24], while another publication reported quantitative conversion of $Os_3(CO)_{11}(NCMe)$ to $Os_3(CO)_{11}(PPh_3)$, representing an overall yield of 80% at best [6]. Essentially quantitative yields of $Os_3(CO)_{11}(PPh_3)$ were obtained by the 1-h UV photolysis of a mixture of $Os_3(CO)_{12}$ and PPh_3 in ethyl acetate, diethyl ether or acetonitrile [5].

The microwave method of CO ligand substitution offers many advantages over the traditional method. It provides the desired complexes in high yields in a much shorter time without the addition of a decarbonylation reagent. There is no need for the extra step of filtering the reaction mixture through silica gel in order to remove excess amine oxide [7]. The microwave method also requires far less solvent: 0.072 L of acetonitrile per mmol of $Os_3(CO)_{12}$ vs. 1.7 L per mmol for the standard preparation of $Os_3(CO)_{11}(NCMe)$. Finally, in contrast to the conventional procedure in which dry, freshly distilled acetonitrile was used and the reaction was carried out under a nitrogen atmosphere, no attempt was made in this work to exclude ambient moisture or air from the reactants and solvents before placing them in the reaction vessel.

In the UV photolysis method, air and moisture must be excluded and the reaction mixture must be kept at 0 °C. A large ratio of 3.0 L of acetonitrile per mmol of $Os_3(CO)_{12}$ is used [5]. Photosubstitution produces a higher yield of $Os_3(CO)_{11}(PPh_3)$, while microwave irradiation gives a better yield of $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{11}(py)$. The microwave method is more convenient, proceeds at a faster rate, and uses far less solvent.

4. Conclusion

Microwave heating allows for the efficient, rapid synthesis of $Os_3(CO)_{11}(NCMe)$ from $Os_3(CO)_{12}$ using less than 5% of the acetonitrile prescribed in previously published methods and eliminating the need for a decarbonylation reagent or an inert gas. After removal of the excess acetonitrile, it is not necessary to purify the residue or isolate $Os_3(CO)_{11}(NCMe)$ before subsequent reactions are performed to produce other monosubstituted triosmium carbonyl cluster complexes in high yields.

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