Cu–C(Cp) bonds are noticeably shorter than in **3b**. This certainly reflects the larger bulk of Cp* as well as the superior donor properties of **1** as compared to those of phosphines.

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Supplementary Material Available: Complete tables of atomic and thermal parameters (7 pages); observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

Synthetic Routes to Alumina-Supported Molybdenum Subcarbonyls. The Effect of the Supported Complex on Olefin Metathesis

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Low-temperature synthetic routes to $Mo(CO)_3$(ads) and its derivatives on aluminum oxide are described. The arene complex (η^6-C_6H_6)$Mo(CO)_3$ loses benzene upon adsorption on partially dehydroxylated Al_2O_3 (CATAPAL SB) to yield $Mo(CO)_3$(ads). This is indistinguishable by infrared spectroscopy and catalytic activity from $Mo(CO)_3$(ads) generated directly from $Mo(CO)_6$. The tris(acetonitrile) complex $Mo(CO)_3(CH_3CN)_3$ reacts in a more complicated fashion with the surface of partially dehydroxylated alumina. One of the products appears to be consistent with the formulation $Mo(CO)_3(CH_3CN)$(ads). All supported carbonyls generated from $Mo(CO)_3(CH_3CN)_3$ are inactive for olefin metathesis.

Introduction

It is well-documented that molybdenum hexacarbonyl reacts with aluminum oxide surfaces to yield supported molybdenum subcarbonyls.[1-3] The reaction of $Mo(CO)_6$ with Al_2O_3 may be accomplished either from the gas phase or from hydrocarbon solution of the carbonyl. The most stable of the subcarbonyls generated fgrom $Mo(CO)_6$ is $Mo(CO)_3$(ads); this is prepared at 100 °C in a flow of ultrapure helium.[1] It is postulated that $Mo(CO)_3$(ads) is stabilized by coordination to surface oxide and/or hydroxide groups depending upon the degree of dehydroxylation of the alumina.[1-4] Infrared spectroscopy has been used to further elucidate the structure of the adsorbed molybdenum tricarbonyl.[3,5,6] The presence of bands below 1600 cm^{-1} in the infrared spectrum has led to some controversy regarding the details of the coordination to the tricarbonyl group by the surface. The following structural features have all been proposed: (i) the presence of a bridging carbonyl interacting with a Lewis acid site on the surface,[7] (ii) a terminal carbonyl interacting with a Lewis acid site on the surface through the carbonyl oxygen,[4] and (iii) a surface hydroxyl group interacting with a carbonyl atom.[3] The materials generated from the adsorption of $Mo(CO)_6$ on aluminum oxide show catalytic activity for a number of reactions including olefin methathesis,[1,8] methanation,[9] and hydrogenation.[10] The olefin metathesis reaction was first recognized over molybdenum catalysts prepared from $Mo(CO)_6$.[11]

The solution chemistry of metal tricarbonyl moieties is well established in the organometallic literature;[12] molybdenum tricarbonyl may be added to a complex synthetically/ either directly from $Mo(CO)_6$ or from $Mo(CO)_3L_3$. The latter compound is typically synthesized thermally from $Mo(CO)_6$ and excess L. Subsequent reactions may then be performed under mild conditions.

In this paper we report the use of $Mo(CO)_3(CH_3CN)_3$ and (η^6-C_6H_6)$Mo(CO)_3$ as precursors to $Mo(CO)_3$(ads) on aluminum oxide. The resulting materials have been investigated via catalytic activity, reaction stoichiometry, and FTIR spectroscopy.

Experimental Section

The complex $Mo(CO)_3(CH_3CN)_3$ was synthesized by refluxing $Mo(CO)_6$ in acetonitrile according to a literature preparation.[13] It was characterized by infrared bands at 1915 and 1783 cm^{-1} (Nujol mull)[13] and satisfactory elemental analysis. The complex (η^6-C_6H_6)$Mo(CO)_3$ was prepared from (η^6-$C_6H_5CH_3$)$Mo(CO)_3$ by refluxing the toluene complex in benzene. The toluene complex was prepared directly from $Mo(CO)_6$ by refluxing in toluene. Removal of the solvent yielded a yellow solid that gave carbonyl bands at 1984 and 1916 cm^{-1} (pentane solvent) corresponding well with literature values.[14]

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The alumina used was CATAPAL SB (Conoco Chemicals, 200 m^2/g, 200–300 mesh); this was calcined in flowing O_2 at 400 °C to remove any organics before use. Adsorption of metal carbonyl complexes onto the alumina was accomplished under ultrapure helium. In a typical experiment, 0.25–0.50 g of the alumina was placed in an ultrapure helium flow reactor system[1] and was heated to 450 °C for 1 h in flowing helium to yield partially dehydroxylated alumina (PDA).[6] The reactor was cooled to room temperature under helium, and a solution containing the desired metal carbonyl complex was injected and slurried with the alumina in flowing helium. The concentration of $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ in pentane was determined by UV spectroscopy.[15] The solvent was evaporated and trapped at −196 °C. The reactor was then heated to activate the material at the desired temperature. Carbon monoxide evolution was measured by the method described by Burwell.[3,9,10,16,17]

Samples for infrared spectroscopy measurements were prepared by sealing the reactor under helium and taking it into a Vacuum Atmospheres drybox where Nujol mulls were made of the material. Infrared spectra were recorded on a Nicolet 5DXB Fourier transform infrared spectrometer.

Metathesis activity was tested by passing standard pulses of propylene in helium through the fludized material in the reactor at the desired temperature. The products were detected by GC as described by Burwell and Brenner.[1]

Results

$Mo(CO)_3(CH_3CN)_3$. The adsorption of $Mo(CO)_6$ onto metal oxides is typically performed in alkane solvents or by direct sublimation of the volatile carbonyl. Alkanes are desirable for the adsorption experiments since they are unreactive toward aluminum oxide at temperatures below 100 °C and may be removed completely from the oxide after adsorption.[18] The tris(acetonitrile) derivative, however, is insoluble in saturated hydrocarbons and does not readily sublime; thus other solvents are necessary for the adsorption experiments. Acetonitrile, diethyl ether, and acetone all dissolve $Mo(CO)_3(CH_3CN)_3$ to give stable solutions of the complex that may be used for the adsorption experiments. Methylene chloride solutions of $Mo(CO)_3(CH_3CN)_3$ decompose at a faster rate than the tris(acetonitrile) complex is adsorbed onto alumina. Methylene chloride has also been observed to yield large background peaks for CO, H_2, and light hydrocarbons.[18]

When the adsorption of $Mo(CO)_3(CH_3CN)_3$ onto alumina is attempted from acetonitreile, none of the molybdenum complex is extracted from solution. Diethyl ether solutions of $Mo(CO)_3(CH_3CN)_3$ are rapidly decolorized by alumina to give a supported molybdenum complex. However, this solvent proved to be inappropriate for further work since the physisorbed ether decomposes to yield ethylene at 100 °C. Acetone solutions of $Mo(CO)_3(CH_3CN)_3$ are also quantitately decolorized by aluminum oxide. Blank runs using pure acetone indicate that no CO or light olefins are produced up to 150 °C. However, acetone does bond very strongly to the surface of alumina[19] and may compete with the metal carbonyl for adsorption sites.

The evolution of carbon monoxide during the adsorption of $Mo(CO)_3(CH_3CN)_3$ from acetone was quantitatively measured as a function of temperature. These results are summarized in Table I. Evolution of CO was found to be independent of the level of loading in the range 0.3–2.1 wt % molybdenum. A reaction time of 2 h was sufficient to quantitate the CO evolution; longer reaction times did not show further loss of carbon monoxide. A temperature of 350 °C is necessary to completely remove all CO from the surface complexes. Although the results from CO evolution measurements do not allow a good definition of an average stoichiometry the following observations can be made. (i) The adsorption process at 25 °C is accompanied by a small but measurable loss of CO. (ii) CO loss increases with temperature until at 150 °C approximately 1 CO/Mo is lost and at 200 °C approximately 2 CO/Mo are lost.

Table I. Carbon Monoxide Evolution during Adsorption of $Mo(CO)_3(CH_3CN)_3$ on Partially Dehydroxylated Alumina

activatn temp, °C	solv	CO/Mo(ads)
25	acetone	0.2 ± 0.1
100	acetone	0.7 ± 0.2
150	acetone	1.1 ± 0.1
200	acetone	1.9 ± 0.1
350	acetone	3.0 ± 0.1

Figure 1. Top spectrum: $Mo(CO)_3(CH_3CN)_3$ adsorbed on PDA from acetone solution, activated 3 h at 25 °C in flowing helium, Nujol mull. Bottom spectrum: $Mo(CO)_3(CH_3CN)_3$ adsorbed on PDA from acetone solution, activated 2 h at 100 °C in flowing helium, Nujol mull.

When activated at 25 °C, the supported complex from $Mo(CO)_3(CH_3CN)_3$ gives the alumina a yellow-brown color reminiscent of $Mo(CO)_3$(ads) generated from $Mo(CO)_6$ at 100 °C.[1,2,9,17] The infrared spectrum of the material generated at 25 °C shows two peaks in the metal carbonyl region at 1907 and 1770 cm^{-1} (Figure 1). These are shifted about 10 cm^{-1} to lower wavenumber from the parent complex. Infrared bands below 1700 cm^{-1} are assigned to reaction products of acetone with aluminum oxide.[19] The infrared results are summarized in Table II.

In contrast to $Mo(CO)_3$(ads) generated from $Mo(CO)_6$ the surface species generated from $Mo(CO)_3(CH_3CN)_3$ is inactive for olefin metathesis.

$(\eta^6\text{-}C_6H_6)Mo(CO)_3$. Arene derivatives of molybdenum carbonyl are typically soluble in hydrocarbon solvent. For example the benzene complex $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ is soluble in benzene and pentane. Both of these solvents were in-

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Table II. Carbonyl Stretching Frequencies for Molybdenum Subcarbonyls Adsorbed on Alumina

source	activatn temp, °C	proposed structure	solv	ν(CO),[a] cm^{-1}	ref
$Mo(CO)_6$	100	$Mo(CO)_3$(ads)	PDA	2030 (w)	3
		1 h, 100 °C	wafer	1994, 1885 (br), 1685, 1584	
$Mo(CO)_6$	100	$Mo(CO)_3$(ads)	PDA	2040 (w)	
		1 h, 100 °C	wafer	2000, 1900 (br), 1680, 1590	7
$Mo(CO)_6$	100	$Mo(CO)_3$(ads)	PDA	2020 (w)	
		4 h, 100 °C	powder	1970, 1929, 1860 (br), 1750 (sh)	this work
			Nujol mull	1570 (sh)	
$Mo(CO)_3(CH_3CN)_3$	25 (3 h)	$Mo(CO)_3(CH_3CN)$	Nujol mull	2005 (w)	this work
			Nujol mull	1907, 1770 (1690, 1625, 1577 (acetone))	
	100 (2 h)		Nujol mull	2004 (w), 1908, 1173, (~1700, 1618, 1574 (acetone))	
	150 (2 h)		Nujol mull	2006 (w), 1910, 1778 (1570 (acetone))	
	200 (2 h)		Nujol mull	2012, 1917, 1786, 1739 (w) (1565 (acetone))	
$Mo(CO)_6$ + NH_3		$Mo(CO)_3(NH_3)$	Nujol mull	1900, 1780 (br), 1760 (sh), 1590 (w)	7
$(\eta^6\text{-}C_6H_6)Mo(CO)3$/pentane	25 ($2^1/_2$ h)	$Mo(CO)_3$(ads)	Nujol mull	1981, 1928, 1861 (br), 1738 (w), ~1580 (sh)	this work
	100 (2 h)	$Mo(CO)_3$(ads)	Nujol mull	2020 (w), 1972, 1929, 1858 (br), 1750 (sh), ~1580 (sh)	this work
$(\eta^6\text{-}C_6H_6)Mo(CO)_3$/ benzene	25 (2 h)	$Mo(CO)_3$(ads)	Nujol mull	1983, 1925, 1851 (br)	this work
				1738	
	100 (1 h)	$Mo(CO)_3$(ads)	Nujol mull	1970, 1933, 1860 (br), 1741 (w), ~1570 (sh)	this work

[a] Abbreviations: w, weak, br, broad; sh, shoulder.

Table III. Carbon Monoxide Evolution during Adsorption of $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ on Partially Dehydroxylated Alumina

activatn temp, °C	solv	CO/Mo(ads)	benzene/ Mo(ads)[a]	$Mo(CO)_6$/Mo- (ads)[a]
25	pentane	0.21 ± 0.1	0.41 ± 0.1	0.0013 ± 0.001
25	benzene	0.04 ± 0.03		ND[b]
100 (2 h)	benzene	0.074 ± 0.08		
100 (7 h)	benzene	0.56		
150 (1 h)	benzene	0.45		

[a] Quantitated by UV spectroscopy. [b] Not detected by UV spectroscopy.

vestigated for the adsorption of $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ onto partially dehydroxylated alumina. The benzene complex is slightly soluble in pentane, and loadings of only 0.4 wt % molybdenum or less could be achieved. To achieve higher loadings, it is necessary to use benzene as the solvent. Partially dehydroxylated alumina rapidly decolorizes both pentane and benzene solutions of $(\eta^6\text{-}C_6H_6)Mo(CO)_3$. Infrared spectroscopy, CO evolution stoichiometry, and catalytic activity measurements were performed on the supported molybdenum carbonyls generated from both solvents to help determine the nature of the supported complex.

The results from the CO evolution experiments are presented in Table III. All adsorptions were performed at 25 °C followed by activation at either 25 or 100 °C. At 25 °C it is evident from the data in Table III that $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ is more efficiently adsorbed from benzene than from pentane. In pentane, adsorption of the benzene complex is accompanied by decomposition to $Mo(CO)_6$ and much of this is removed from the reactor. The CO evolved when the adsorption is performed from pentane is very likely due to adsorption of the $Mo(CO)_6$ generated in situ onto the alumina. When the adsorption is performed from benzene, no $Mo(CO)_6$ could be detected by UV spectroscopy and virtually no CO is evolved at 25 °C. At a temperature where $Mo(CO)_3$(ads) should be stable, i.e., 100 °C, the adsorbed carbonyl generated from $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ loses CO very slowly, consistent with the formation of the supported tricarbonyl.

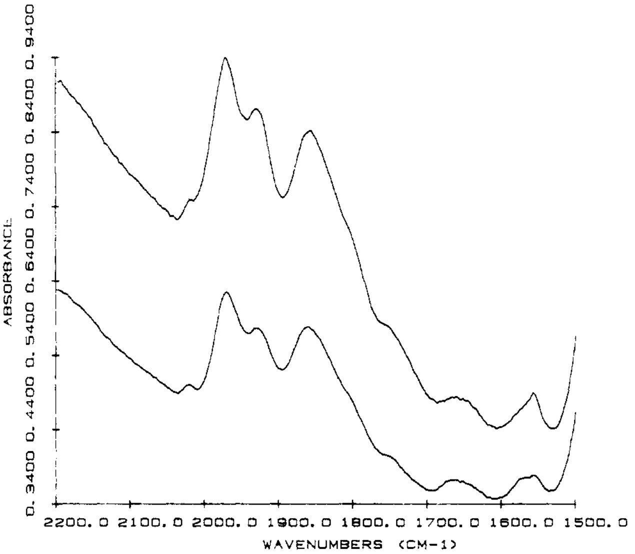

Figure 2. Top spectrum: $Mo(CO)_3(\eta^6\text{-}C_6H_6)$ adsorbed on PDA from pentane solution activated 2 h at 100 °C in flowing helium, active for propylene methathesis, Nujol mull. Bottom spectrum: $Mo(CO)_6$ adsorbed on PDA from pentane solution, activated 3 h at 100 °C in flowing helium, active for propylene methathesis, Nujol mull.

The infrared spectra for the supported carbonyls generated from $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ and $Mo(CO)_6$ are remarkably similar. These are shown as Nujol mulls in Figure 2, and the band positions are given in Table II. Two major bands at 1970 and 1860 cm^{-1} are observed in both cases. These are similar to those reported by Burwell et al.[3,9,10] and Howe[6,7] but shifted slightly to lower wavenumber. Bands below 1600 cm^{-1} for the adsorbed tricarbonyl have been assigned in several different ways as discussed in the introduction. The spectra shown in Figure 2 were obtained on samples prepared as mulls and not in situ on pressed pellets as Burwell[3] and Howe[7] report. At the present time we will not add further speculation as to the origin of these bands. For the spectra shown in Figure 2 the bands at 1655 and 1556 cm^{-1} are present on the alumina itself.

The supported $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ complexes, generated from either pentane or benzene solutions, show similar activity for the metathesis of propylene at a temperature of about 50 °C as supported complexes generated from $Mo(CO)_6$.

Propylene Metathesis. The activity of the supported carbonyls for propylene metathesis is summarized in Table IV. These results were obtained in a pulsed reactor over a fludized bed of the alumina-supported carbonyl. The activity is listed as the percent conversion of propylene in

Table IV. Activity for Propylene Metathesis at 100 °C for Various Catalysts

	cat. precursor	activation temp, °C	wt %	activity,[a] %	turnover,[b] s^{-1}
I	$Mo(CO)_6$/pentane	100	0.92	8.9 at 54 °C	0.0056
	above + acetone	100		not active at 54 °C	
II	$Mo(CO)_6$/pentane	100	1.3	7.6 at 54 °C	0.0033
	above + benzene	100	1.3	8.6 at 53 °C	0.0038
III	$Mo(CO)_6$/acetone	100	1.1	not active at 100 °C	
IV	$Mo(CO)_3(CH_3CN)_3$/acetone	100	0.54	not active at 100 °C	
V	$(\eta^6\text{-}C_6H_6)Mo(CO)_3$/pentane	100	0.79	10.7 at 55 °C	0.0079
VI	$(\eta^6\text{-}C_6H_6)Mo(CO)_3$/benzene	100	0.76	9.7 at 52 °C	0.0074
	$Mo(CO)_6$/pentane[c]	100	0.56	0.8 at 53 °C	0.013[d]

[a] Activities are reported as percent conversion of propylene for the first pulse. [b] Turnover is reported as moles of propylene consumed per mole of molybdenum per second. The contact time of a pulse in the reactor used in this work was measured to be 5.5 s. [c] Reference 20. [d] Reported for a contact time of 1.6 s.

the first pulse; also shown is the turnover per pulse. For comparison the data of Brenner is also shown under similar conditions.[20]

Active catalysts are obtained from both $Mo(CO)_6$- and $(\eta^6\text{-}C_6H_6)Mo(CO)_3$-derived molybdenum subcarbonyls. Furthermore the activities of these catalysts on a per molybdenum basis are very similar. However, the supported carbonyls generated from $Mo(CO)_3(CH_3CN)_3$ are inactive for metathesis. Poisoning experiments on an active metathesis catalyst show that both acetonitrile and acetone are poisons for the catalysis whereas benzene has no effect on the catalysis. Thus materials generated from either acetonitrile or acetone solvents or from carbonyl complexes containing nitrile ligands will be inactive for metathesis.

The metathesis reaction was run to compare the activities of supported carbonyls synthesized by different methods. For up to five pulses the activity remains constant; however, a maximum of only 0.1 turnovers per molybdenum is observed. Long-term catalyst activity has been demonstrated for these materials in continuous-flow experiments although turnovers are not reported.[11] In recycling batch reactions for propylene matathesis a total of 1.6 turnovers has been obtained with no loss of activity.[21]

Discussion

The attempted reactions for generating $Mo(CO)_3(ads)$ on alumina are shown in eq 1 and 2. Although there is

$$Mo(CO)_3(CH_3CN)_3 + Al_2O_3 \rightarrow Mo(CO)_3(ads) + 3CH_3CN \quad (1)$$

$$(\eta^6\text{-}C_6H_6)Mo(CO)_3 + Al_2O_3 \rightarrow Mo(CO)_3(ads) + C_6H_6 \quad (2)$$

a great deal of precedent for these reactions in the organometallic literature the results presented above indicate that acetonitrile is not an appropriate leaving group when using the surface of aluminum oxide as a potential ligand.

When the reaction represented by eq 2 is performed in pentane, some decompositon of $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ to yield $Mo(CO)_6$ is observed. Also 0.25 equiv of CO are observed per adsorbed Mo at 25 °C. Carbon monoxide evolution is not predicted by eq 2 and is most likely due to direct adsorption of the $Mo(CO)_6$ generated in situ. A similar quantity of CO is observed during the adsorption of $Mo(CO)_3(CH_3CN)_3$ from acetone (eq 1) at 25 °C. Although $Mo(CO)_6$ was not observed in this case, a pathway involving formation of $Mo(CO)_6$ cannot be ruled out. Infrared spectroscopy (vide infra) suggests that some of the tris(acetonitrile) complex reacts at 25 °C to lose only two acetonitrile ligands. Furthermore addition of CH_3CN to $Mo(CO)_3(ads)$ generated from $Mo(CO)_6$ results in a surface species that has a similar infrared spectrum to that of $Mo(CO)_3(CH_3CN)_3$ adsorbed on alumina.

The reaction stoichiometry predicted by eq 2 is most closely approximated when $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ is adsorbed from benzene. Although benzene loss could not be quantitated in this case, the combination of observations, (i) virtually no CO loss at 25 °C, (ii) no $Mo(CO)_6$ formed, and (iii) complete extraction of $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ from solution, suggest that eq 2 is a good representation of the adsorption process. Furthermore the adsorbed complex loses CO very slowly at 100 °C, conditions where $Mo(CO)_3(ads)$ is expected to be stable. Under similar conditions the adsorbed carbonyl from $Mo(CO)_3(CH_3CN)_3$ loses CO much more rapidly. Finally the infrared spectrum of $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ adsorbed on alumina at 25 °C is nearly identical with the spectrum obtained for $Mo(CO)_6$ on alumina activated at 100 °C. Thus there is good evidence that eq 2 is a viable pathway to adsorbed $Mo(CO)_3$ under ambient conditions.

In the infrared spectrum two principal CO stretches are observed for $Mo(CO)_3(ads)$ on PDA by Laniecki and Burwell.[3] These occur at 1994 and 1885 cm^{-1}. Also a band at 1584 cm^{-1} was assigned to the interaction of a terminal carbonyl with a surface hydroxyl group on the surface.[3] Kazusaka and Howe[7] report values of 2000 and 1900 cm^{-1} in the terminal carbonyl region and found that adsorption of ammonia causes these peaks to shift to 1900 and 1780 cm^{-1}. The authors speculate the shift to be caused by ammonia coordination to molybdenum to form $Mo(CO)_3(NH)_3(ads)$. Also, after partial removal of the adsorbed ammonia Kazusaka and Howe observe a further 20 cm^{-1} shift that they attribute to a solvent effect. In the case of $Mo(CO)_3(CH_3CN)_3$ adsorbed as γ-alumina, the presence of two carbonyl stretches is consistent with a tricarbonyl complex being formed on the surface. However, the supported complex appears to retain a coordinated nitrile ligand, as suggested by the similarity of the infrared bands at 1907 and 1770 cm^{-1} with those reported for $Mo(CO)_3(NH_3)(ads)$. Thus the predominant adsorbed species at 25 °C from $Mo(CO)_3(CH_3,cN)_3$ may be represented as $Mo(CO)_3(CH_3CN)$. After heating, excess nitrile and acetone solvent are removed from the surface and the bands shift to 1917 and 1786 cm^{-1} which may be due to a solvent effect. This assignment is supported by an experiment in which $Mo(CO)_3(ads)$ on PDA from $Mo(CO)_6$ was reacted with acetonitrile and activated at 100 °C. The resulting infrared spectrum has two CO stretches at 1908 and 1772 cm^{-1} and a small peak at 2020 cm^{-1} in good agreement with the bands obtained by direct adsorption of $Mo(CO)_3(CH_3CN)_3$. Furthermore addition of CH_3CN to an active metathesis precursor, i.e. $Mo(CO)_3(ads)$ from $Mo(CO)_6$, poisoned the catalyst for propylene metathesis. When $Mo(CO)_3(ads)$ from $Mo(CO)_6$ was reacted with acetone and activated at 100 °C, the IR spectrum also

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shows two peaks at 1906 and 1768 cm^{-1} and a small peak at 2020 cm^{-1}. Likewise in this case the catalyst was poisoned for propylene metathesis. Alternatively when $Mo(CO)_6$ is reacted with the alumina from acetone solutions and activated at 100 °C, two major peaks are present in the IR spectrum at 1905 and 1771 cm^{-1} and a smaller peak is at 2036 cm^{-1}, but the material is inactive for metathesis. Thus acetone not only prevents the formation of catalytically active $Mo(CO)_3$(ads) but also poisons the active catalyst as acetonitrile did. It appears that acetone is able to coordinate to molybdenum to cause the large shifts observed in the IR spectrum as proposed for acetonitrile. Therefore the species formed in the reaction of $Mo(CO)_3(CH_3CN)_3$ with γ-alumina from acetone solution is postulated to be $Mo(CO)_3(CH_3CN)$(ads). This decomposes at elevated temperatures as evidenced by CO evolution. In addition to coordination to the molybdenum tricarbonyl acetone and acetonitrile are known to interact strongly with partially dehydroxylated surfaces, and this may also contribute to the poisoning of the metathesis activity.

The alumina-supported molybdenum carbonyls generated from $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ and $Mo(CO)_6$ are indistinguishable on the basis of infrared spectroscopy and olefin metathesis activity. Thus the use of an arene ring as a leaving group is demonstrated as a viable low-temperature reaction pathway to supported metal complexes.

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Registry No. $(\eta^6\text{-}C_6H_6)Mo(CO)_3$, 12287-81-9; $(\eta^6\text{-}C_6H_5CH_3)Mo(CO)_3$, 12083-34-0; $Mo(CO)_6$, 13939-06-5; $Mo(CO)_3(CH_3CN)_3$, 15038-48-9; propylene, 115-07-1.

Synthesis and Crystal and Molecular Structures of $M(OAr')_2(CH_2\text{-py-6Me})_2$ (M = Hf, Th; OAr′ = 2,6-Di-*tert*-butylphenoxide; CH_2-py-6Me = 2-(6-Methylpyridyl)methyl), Complexes Containing Two C,N-Chelating Pyridyl–Methyl Ligands

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The reaction of the tetrachlorides MCl_4 (M = Hf, Th) with excess of $LiCH_2$-py-6Me ($LiCH_2$-py-6Me = (2-(6-methylpyridyl)methyl)lithium) leads to the sparingly soluble dialkyls $MCl_2(CH_2\text{-py-6Me})_2$ (M = Hf, Th). Further treatment of these materials with LiOAr′ (>2 equiv; OAr′ = 2,6-di-*tert*-butylphenoxide) leads to the pale yellow, crystalline compounds $M(OAr')_2(CH_2\text{-py-6Me})_2$ (M = Hf, Th) which are soluble in hydrocarbon solvents and are more amenable to study. Structural studies show both the hafnium and thorium compounds to be isomorphous and isostructural, the metal being found to be six-coordinate with both pyridyl–methyl ligands C,N-chelating. Some distortions of the coordination environment are evident, presumably due to the formation of two strained, four-membered rings. Although the M–N(py) distances do not appear to be elongated, solution studies indicate that dissociation of pyridine groups is facile. However, ^{13}C NMR data are supportive of the idea that the ligands remain predominantly, C,N-bound in solution. $Hf(OAr')_2(CH_2\text{-py-6Me})_2$ crystallizes in space group $I2/a$ with a = 16.980 (4) Å, b = 10.438 (1) Å, c = 21.865 (5) Å, β = 106.77 (1)°, Z = 4, and d_{calcd} = 1.435 g cm^{-3} at −157 °C. $Th(OAr')_2(CH_2\text{-py-6Me})_2$ also crystallizes in space group $I2/a$ with a = 16.826 (5) Å, b = 10.679 (1) Å, c = 22.491 (5) Å, β = 106.04 (2)°, Z = 4, and d_{calcd} = 1.462 g cm^{-3} at 22 °C.

Introduction

The ability of donor ligands and solvents to stabilize high-valent early-transition-metal homoleptic alkyl compounds was recognized by early synthetic workers in this branch of organometallic chemistry.[2,3] Hence thermally unstable, even sometimes explosive, peralkyls can be stabilized by chelating ligands such as bpy and dmpe.[4] The field of cyclometalation chemistry which has developed over the last 20 years owes much to the enhanced stability imparted to the metal–carbon bond formed in these reactions by the heteroatom donor in the resulting metallacycle.[5-7] Work by Manzer[8] and others[9] has demonstrated

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