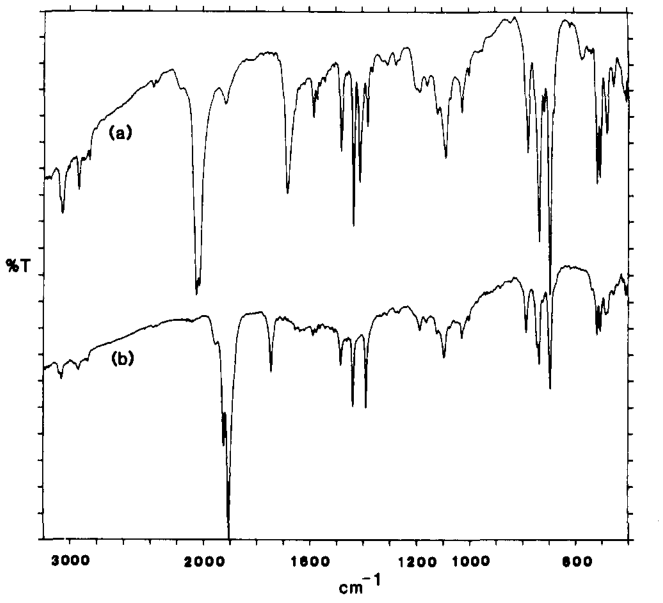
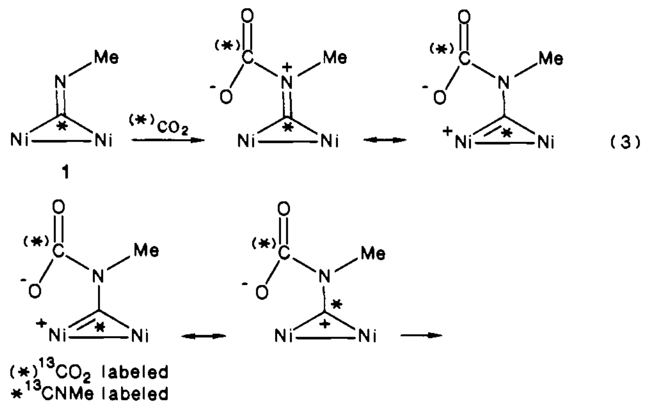
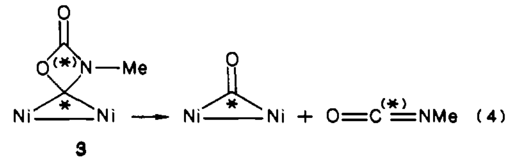


Figure 4. (a) FTIR spectrum of >99% ^{13}C-enriched $Ni_2(^{13}CNMe)_3(dppm)_2$, $1(^{13}C)$. (b) FTIR spectrum of the product obtained by reaction of $1(^{13}C)$ with $^{12}CO_2(l)$, corresponding to >99% ^{13}C-enriched $Ni_2(^{13}CO)_3(dppm)_2$, $4(^{13}C)$.

μ-CNMe ligand. In particular, the results obtained from the reaction of $1(^{13}C)$ with $^{12}CO_2(l)$ unambiguously establish that the coordinated CO carbon atoms of **4** are derived from the methyl isocyanide ligands of **1**. The initial fate of the carbon dioxide carbon atom very likely is methyl isocyanate formation. The results are consistent with the mechanism depicted in eq 3 and 4. Presumably, the *N,N'*-dimethyl carbodiimide results from the increased reactivity of methyl isocyanate relative to CO_2 in the O/NMe interchange reaction. Indeed, **1** does react with isocyanates to give **4** and the corresponding carbodiimides. We suspect the role of the Na^+ ion in catalyzing the formation of **3** in fluid solution at 1 atm of CO_2 is to stabilize charge-separated zwitterionic carbyne intermediates, prior to cyclization leading to **3**, eq 4. A similar mode of CO_2 activation by Li^+ has recently been reported for $W(CO)_5^{2-}$.[20] Nucleophilic cyclization to **3** has





precedence in the observation that the related complex, $[Ni_2(\mu\text{-}(CNMe)(Me))(CNMe)_2(dppm)_2]^+$, does undergo nucleophilic attack at the carbyne carbon by H^-.[4,19] The CO_2 cycloadduct **3** either can revert to **1** with CO_2 loss or form methyl isocyanate and CO. However, we have not isolated methyl isocyanate or the mono- and dicarbonyl intermediates leading to **4**. This suggests that the intermediates may be significantly more reactive than **1** and CO_2 in the O/NMe interchange reaction. The apparent substitution of three isocyanide ligands by carbon monoxide, eq 2, with complete retention of the metal–carbon bonding framework is unprecendented.

Acknowledgment. This work was supported by NSF (CHE-8411836) and DOE (DE-FG22-84PI70791). D.L.D. acknowledges a David Ross Fellowship. The PDP 11/34 computer and X-ray Structure Solution Package in the Department of Chemistry were purchased with funds from the NSF Chemical Instrumentation Program (CHE-8204994) and the Monsanto Fund.

Supplementary Material Available: Tables of crystal data and conditions for data collection, positional parameters, general temperature factors, and bond distances and angles (15 pages); tables of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

---

[20] Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 7606.

Organic Residues Introduced during Metal Oxide Functionalization

C. S. Goldstein, K. D. Weiss, and R. S. Drago*

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611. *Received March 24, 1986*

Abstract: Silica and alumina supports have been functionalized with reagents of the general formula $(C_2H_5O)_3Si(CH_2)_nX$ where X is a donor group capable of coordinating to metal complexes. The attachment of iridium clusters to the phosphinated support has been shown to lead to $(AL)\text{-}PPh_2Ir_4(CO)_{11}$, $(AL)(\text{-}PPh_2)_2Ir_4(CO)_{10}$, and $(AL)(\text{-}PPh_2)_3Ir_4(CO)_9$ ((AL) is the abbreviated form of $Al_2O_3\text{-}O\text{-}Si(CH_2)_2$). The attached iridium cluster reacts with a gaseous mixture of H_2/CO/HCl to form products which result from organic residues introduced during functionalization of the oxide. Failure to recognize this problem leads to adventitious carbon sources in catalytic processes that can lead to incorrect conclusions, and reaction of these materials with HCl enables one to detect these organic residues and to clean the surface. A reaction scheme for the decomposition of ethoxy groups of the phosphinosilane to methyl chloride is included.

The recent literature contains many examples of silica and alumina supports that have been functionalized with the reagents of the general formula $(C_2H_5O)_3Si(CH_2)_nX$ where X is a donor group capable of coordinating to metal complexes.[1,2] A thorough study of the hydrolysis of ethoxy groups by surface silanol groups has been reported along with the effects of curing these reagents.[3]

---

[1] Evans, J.; Gracy, B. *J. Chem. Soc., Chem. Commun.* **1980**, 852.

Table I[a]

	support	preparation	drying procedure (°C, h)	gas flow	products (°C)	mol prod s^{-1} g $catalyst^{-1}$
1	(AL)–$PPh_2Ir_4(CO)_{11}$ and (AL)(–$PPh_2)_2Ir_4(CO)_{10}$	2-methoxyethanol under 40 psi CO at 90 °C from $Ir(CO)_2Cl\cdot$*p*-toluidine	vacuum 40, 12	$H_2/CO/HCl$	CH_3CH_2Cl	$\sim 10^{-12}$
					CH_3Cl at 75	$\sim 10^{-10}$
2	(AL)–PPh_2 or (SG)–PPh_2	stirred with 2-methoxyethanol under 40 psi CO at 90 °C	vacuum 40, 12	$H_2/CO/HCl$	CH_3Cl at 75	$\sim 10^{-10}$
			vacuum 80, 12	$H_2/CO/HCl$	CH_3Cl at 75	$\sim 10^{-10}$
3	Al_2O_3 or SiO_2	2-methoxyethanol under 40 psi CO at 90 °C	vacuum 40, 8	$H_2/CO/HCl$	CH_3Cl at 60	$\sim 10^{-10}$
4	(AL)–PPh_2	reflux in toluene by using $(CH_3O)_3SiC_3H_6PPh_2$	vacuum 40, 12	H_2/CO	CH_3OH at 60	$\sim 10^{-11}$
				$H_2/CO/HCl$	CH_3Cl at 60	$\sim 10^{-11}$
5	(AL)–PPh_2	reflux in toluene by using $(CH_3CH_2O)_3Si–C_2H_4PPh_2$	vacuum 80, 12	H_2/CO	CH_3CH_2OH at 60	$\sim 10^{-10}–10^{-11}$
				$H_2/CO/HCl$	CH_3CH_2Cl at 60	$\sim 10^{-10}–10^{-11}$
					CH_3CH_2Cl	$\sim 10^{-10}–10^{-11}$
					CH_3Cl at 100	$\sim 10^{-10}–10^{-11}$
				H_2/HCl	CH_3CH_2Cl	$\sim 10^{-10}–10^{-11}$
					CH_3Cl at $T > 100$	$\sim 10^{-11}–10^{-12}$
6	(AL)–PPh_2	reflux in benzene by using $(CH_3CH_2O)_3–SiC_2H_4PPh_2$	vacuum 80, 12	H_2/CO	CH_3CH_2OH at 60	$\sim 10^{-10}$
				$H_2/CO/HCl$	CH_3CH_2Cl at 100	$\sim 10^{-10}–10^{-11}$
				H_2/HCl	CH_3CH_2Cl	$\sim 10^{-10}–10^{-11}$
					CH_3Cl at $T > 150$	$\sim 10^{-13}$

[a] In 1 and 2, (AL)–PPh_2 was first prepared from reaction of Al_2O_3 with $(CH_3CH_2O)_3Si–C_2H_4PPh_2$ refluxing benzene. (SG)–PPh_2 was prepared in a similar manner by using SiO_2. In 1, 0.31% iridium loading.

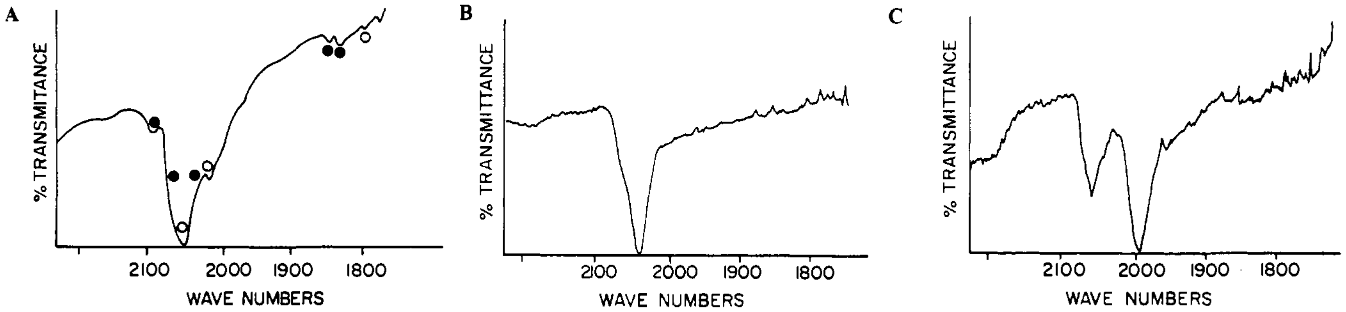


Figure 1. (A) Infrared spectra of the iridium catalyst prepared in toluene: ●, (AL)–$PPh_2Ir_4(CO)_{11}$ absorptions; ○, (AL)(–$PPh_2)_2Ir_4(CO)_{10}$ absorptions; 1.18% iridium. (B) Infrared spectra of the iridium species supported on alumina functionalized with the ethoxy silane after exposure to a gaseous mixture of $H_2/^{12}CO/HCl$ at 75 °C: $\nu_{^{12}CO} = 2045$ cm^{-1}. (C) Infrared spectra of the iridium species supported on alumina functionalized with the ethoxysilane after exposure to a gaseous mixture of $H_2/^{13}CO/HCl$ at 75 °C. Substitution by ^{13}CO is evident from the shifted carbonyl frequencies: $\nu_{^{13}CO}$ 1995 cm^{-1} = $\nu_{^{12}CO}$ 2045 cm^{-1}, $\nu_{^{12}CO}$ = 2066 cm^{-1}.

We became interested in the attachment of metal clusters to silica gel and alumina via the above type of functionalizing agent in which X is a $-P(C_6H_5)_2$ group. Such systems are of interest as potential catalysts for isomerizations, hydrogenations, hydroformylation, CO reduction, etc., for as previously discussed the hybrid catalysts offer many of the advantages of both homogeneous and heterogeneous systems.[4] The attachment of iridium clusters to the phosphinated support has been shown to lead to (SG)–$PPh_2Ir_4(CO)_{11}$, (SG)(–$PPh_2)_2Ir_4(CO)_{10}$, and (SG)(–$PPh_2)_3Ir_4(CO)_9$ ((SG) is the abbreviated form of silica gel).[5-7] In this work we show that the functionalization procedure leads to the incorporation of organic residues on the surface of the inorganic oxide support that are very difficult to remove. Failure to recognize this problem leads to adventitious carbon sources that can lead to incorrect conclusions. We have found that reaction of these materials with HCl enables one to detect and remove these organic residues.

Experimental Section

Materials. The support material was Fisher, acid Brockman Activity I (80–200 mesh) alumina, or Davidson grade no. 62 silica gel. This alumina was determined to have a specific area of 180 m^2/g.[8] The silica gel had a specific area of 340 m^2/g, a pore diameter of 14 mm, and a pore volume of 1.1 cm^3/g. All supports were dried at 140 °C prior to use. The phosphino silane $(alkoxy)_3Si(CH_2)_xPPh_2$ where alkoxy = (CH_3O) or (CH_3CH_2O) and x = (2 or 3) was purchased from Petrarch Systems, Inc. The benzene and toluene (Fisher Scientific) were dried, distilled over CaH_2, and stored over 4Å molecular sieves. The 2-methoxyethanol (Kodak, scintillation grade) was used without further purification.

Hydrogen was purchased from Airco and had a purity of 99%. The CO (CP grade), 99.5%, and the HCl (isoelectronic grade), 99.99%, were purchased from Matheson Gas Products. All gases were used without further purification.

Support Functionalization and Cluster Attachment. The various preparations and drying procedures of the functional supports that were conducted are summarized in Table I. In general, the supports were functionalized through a simple condensation reaction of the alkoxy groups of the phosphino silane with the hydroxyl groups on the supports surface. In each preparation, the support was allowed to react with the phosphino silane (1.25 × 10^{-3} mol of phosphine per g of support) for ~12 h in refluxing benzene or toluene. The functionalized support was collected by filtration, washed several times with benzene or toluene, and dried as previously summarized. In the supports where the tetrairidium cluster was attached, the products consisted of the mono[$Ir_4(CO)_{11}PPh_2(CH_2)_2$–] and disubstituted [$Ir_4(CO)_{10}(PPh_2(CH_2)_2–)_2$] clusters. Confirmational assignments were made by infrared spectroscopy and agree with those previously reported.[5-7,9] The infrared spectrum of the mixture of monosubstituted and disubstituted clusters is shown in Figure 1A: $\nu_{(CO)}$ = 2083, 2039, 2005, 1845, 1827 cm^{-1}; reported[6,7] for the monosubstituted cluster $\nu_{(CO)}$ = 2090, 2061, 2023, 1845, 1825 cm^{-1}; reported[7] for the disubstituted cluster $\nu_{(CO)}$ = 2074, 2050, 2017 cm^{-1}.

Catalytic Studies. Runs were conducted by using ~1.0 g of support in a fixed bed flow reactor system. Up to 2 psi of a gaseous mixture of $H_2/CO/HCl$ (2:1:0.5), H_2/CO (2:1), or H_2/HCl (2:0.5) were used as feed. Once the proper gas mixture was established, the support material was then heated. Temperatures were increased and maintained between

---

(2) Evans, J.; Gracy, B. *J. Chem. Soc., Chem. Commun.* **1983**, 247.

(3) Waddell, T. G.; Leyden, D. E.; De Bello, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 303.

(4) Zwart, J.; Snel, R. *J. Molec. Catal.* **1985**, *30*, 305.

(5) Castrillo, T. et al. *Inorg. Chim. Acta* **1980**, *44*, 239.

(6) Lieto, J.; Rafalko, J. J.; Gates, B. C. *J. Catal.* **1980**, *62*, 149.

(7) Studer, D. W.; Schrader, G. L. *J. Mol. Catal.* **1980**, *9*, 169.

(8) Holbrook, M. *Dow Chemical Company*, personal communication, 1985.

(9) Stuntz, G. F.; Shapeley, J. R. *Inorg. Chem.* **1976**, *15*, 1995.

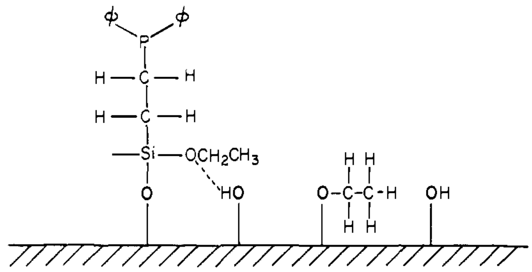


Figure 2. Structure of the ethoxy surface species formed during functionalization of the aluminum oxide.

50 to 150 °C by using a model 123-8 Lindberg thermostated tube furnace.

Instrumentation. Gaseous products were detected by gas chromatography by using a Model 940 FID Varian chromatograph equipped with a 1/8 in. × 8 ft stainless steel Porapak Q column. The column temperature was maintained at 130 °C. All product assignments were confirmed by GC mass spectrometry. Samples were run by using a AEI MS 30 mass spectrometer equipped with a KOITOS DS55 data station. The system was equipped with a PYE Unicam 104 gas chromatograph containing a 1/4 in. × 5 ft Porapak Q column. All infrared spectra were obtained as Nujol mulls by using a Nicolet model 5DXB FTIR spectrometer.

Results and Discussion

The series of experiments contained in Table I were carried out in an attempt to elucidate the carbon products that could result from the organic residues left on the inorganic oxide support after functionalization. The reaction conditions employed were those expected to lead to CO reduction in a catalytic system. For quantitative purposes the number of mol of products per s per g of catalyst has been included.

An alumina supported phosphine catalyst is coordinated to an iridium cluster to form Al_2O_3–O–$Si(CH_2)_2PPh_2Ir_4(CO)_{11}$ (abbreviated as (AL)–$PPh_2Ir_4(CO)_{11}$) and (AL)$(-PPh_2)_2Ir_4(CO)_{10}$ according to a literature procedure.[6,7,9] This material is prepared in 2-methoxyethanol and vacuum dried at 40 °C for 12 h. When a mixture of $H_2/CO/HCl$ is passed over this catalyst or one is formed from reacting the phosphine substituted support with $Ir_4(CO)_{12}$ in toluene, formation of ethyl and methyl chloride is detected at 75 °C. In order to determine if these products result from the reduction of CO, labeled CO was introduced into the system. As can be seen in Figure 1, extensive substitution of CO by ^{13}CO occurs in the bound iridium species. In spite of this only 1.4% of ^{13}C above natural abundance is detected in the methyl chloride found in the reaction products, and no ^{13}C was incorporated into ethyl chloride. In order to determine the source of methyl halide, experiments 2 and 3 in Table I were carried out clearly showing that CH_3Cl is produced from 2-methoxyethanol incompletely removed by vacuum drying and cleaved by HCl on the alumina surface.

In an attempt to investigate the possibility that alkoxy groups from the functionalizing agent could lead to methyl chloride, alumina was functionalized with $(CH_3O)_3SiC_3H_6P(C_6H_5)_2$ and $(C_2H_5O)_3SiC_2H_4P(C_6H_5)_2$ in toluene and benzene solvent (experiments 4–6). In all instances the alcohol corresponding to the alkoxy group was detected when H_2 and CO were passed over the functional support at 60 °C, and the alkyl chloride was obtained when the gas mixture of $H_2/CO/HCl$ was passed over the same support. When this gas mixture of $H_2/CO/HCl$ was passed over the support functionalized with $(C_2H_5O)_3SiC_2H_5P(C_6H_5)_2$ in toluene at 100 °C, methyl chloride was observed, but this product was not detected when benzene was used instead of toluene during the functionalization procedure. The formation of methyl chloride in addition to ethyl chloride was detected in the benzene preparation when H_2 and HCl was passed over the solid at temperatures greater than 150 °C.

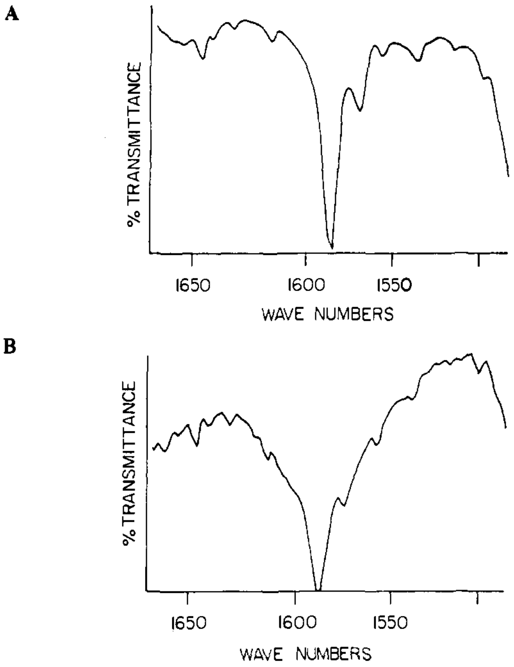


Figure 3. (A) Infrared spectra of $(CH_3CH_2O)_3SiCH_2CH_2PPh_2$ film showing the phenyl group resonances: ν_{phenyl} = 1587, 1572 cm^{-1}. (B) Infrared spectrum of (AL)–PPh_2 indicating that the phenyl groups remain present after being exposed to $H_2/CO/HCl$ at 100 °C: ν_{phenyl} = 1587, 1572 cm^{-1}.

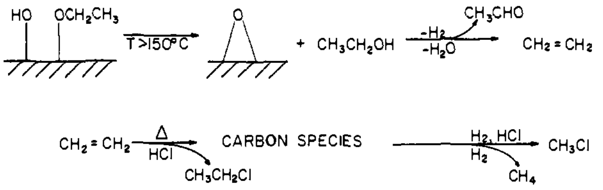


Figure 4. Schematic representation of the decomposition of ethoxy groups at elevated temperatures.

These observations are interesting in view of the reaction reported by Waddell et al.[3] and Studer and Schrader.[7] In these articles, these alkoxy groups in (alkoxy)$_3Si(CH_2)_xPPh_2$ are reported to be hydrolyzed off of the silicon in the course of functionalization producing the alcohol and forming hydroxyl groups bound to the inorganic oxide. If this hydrolysis occurs, the alumina surface retains the alcohol or alkoxy groups as shown in Figure 2, because these products yield alkyl halides when reacted with HCl at 60 °C and above (experiments 3–6). When ethoxysilanes are used in the functionalization, ethyl chloride is detected at 60 °C, and both ethyl and methyl chloride are seen above 100 °C (experiment 5). Although at temperatures of 100 °C methyl chloride is produced from the toluene preparation (experiment 5), the same preparation in benzene (experiment 6) did not produce methyl chloride at this temperature. In the benzene preparation, methyl chloride production was observed only at temperatures above 150 °C. We suspect that methyl chloride is produced from the cracking of toluene in experiment 5. The detection of CH_3Cl above 150 °C in experiment 5 is believed to occur from decomposition of the ethoxy groups present on the phosphino silane, or on the alumina surface and cracking of benzene does not appear to occur.

The only other carbon source besides the alkoxy groups which could be responsible for the formation of the ethyl chloride is the $(CH_2)_x$ chain present in the phosphinosilane linkage, $(CH_3CH_2O)_3Si(CH_2)_xPPh_2$. It is possible that decomposition of this linkage under the reaction conditions employed could account for the formation of the observed ethanol and ethyl chloride. However, continued existence of the phosphino silane linkage after exposure to $CO/H_2/HCl$ at 100 °C is indicated by the phenyl group resonances observed by infrared spectroscopy are shown in Figure 3.

The reaction scheme corresponding to the decomposition of the ethoxy groups from the phosphinosilane to form CH_3Cl (experiment 6) is represented in Figure 4. In this experiment, the

J. Am. Chem. Soc. 1987, 109, 761-768

support was prepared in benzene and in contrast to the preparations by using toluene, and 2-methoxyethanol cracking of the solvent is not expected to occur. In this scheme, reaction of the adsorbed ethoxy groups would lead to ethanol production. Dehydration of coordinated ethanol or ethoxy groups would result in the formation of ethylene while dehydrogenation of ethanol produces acetaldehyde. Acetaldehyde is detected in the early phases of our experiments by GC and GC/MS. Ethylene is detected throughout the experiment as a minor byproduct. As shown in Figure 4, ethylene may then react with HCl to produce ethyl chloride which is the major product from the reaction of ethanol or ethoxy groups with HCl. Ethylene may be cracked over the alumina surface producing carbon species. Reaction of the carbon species with hydrogen and HCl would account for the methane and methyl chloride observed in our experiments with the ethoxy phosphino silane. All of these reactions are further complicated by reactions involving the intermediate species. Evidence for such a scheme is supported by reports in the literature. Several reports indicate that ethanol can be converted over inorganic oxides to ethylene,[10-12] ethane,[10] and acetaldehyde[13,14] all of which were observed as minor products in our reactions. It is generally recognized that olefins are an important source of carbon formation involved in catalytic cracking.[15] Reports indicate that over a metal surface ethylene may decompose to carbon atoms via an acetylene intermediate.[16,17] We believe similar chemistry is occurring whereby decomposition of ethoxy groups eventually lead to the formation of methyl chloride.

When alumina was functionalized with $(CH_3CH_2O)_3SiC_2H_4P(C_6H_5)_2$, we found that the adventitious carbon could be removed by passing HCl gas over the functionalized support at 150 °C until ethyl chloride was no longer observed in the exit gas. It was a concern that after this treatment the support would lead to the decomposition of metal carbonyls, but we were able to show that the tetrairidium cluster could be absorbed onto the alumina when $Ir_4(CO)_{12}$ is reacted with the solid in refluxing benzene. Infrared showed that the cluster remained intact. When this catalyst was then reacted with H_2, CO, and HCl at 70 °C, no products corresponding to those expected from the reduction of CO or from organic residues introduced during synthesis were observed.

Acknowledgment. We appreciate the generous support of this research by Dow Corning Corporation and thank Dr. R. King for his guidance with the GCMS.

---

(10) Barrocas, H. V.; Da Silva, C. M.; Coutinho, A. R.; Baptista, J. *Ger. Offen.* 2834699, 1979.

(11) Andelson, J. R.; Rajadhayaksha, R. A.; Weiss, D. E.; Mole, T.; Wilshier, K. G.; Whiteside, J. A. *Eur. Pat. Appl.* 22640, 1981.

(12) Garmashev, Y. M.; Vladyko, L. I.; Trojchimets, A. I. *Vesti Akad. Nauk BSSR, Ser Khim Nauuk* **1981**, *26*, 175; *Chem. Abstr.* **1981**, *95*, 13460.

(13) Kochar, N. K.; Marcell, R. L. *Chem. Eng.* **1980**, *87*, 80.

(14) Franckaerts, J.; Froment, G. F. *Chem. Eng. Sci.* **1964**, *19*, 807.

(15) Corma, A.; Wojciechowski, B. W. *Catal. Rev. - Sci. Eng.* **1985**, *27*, 29.

(16) Chester, M. A.; Hopkins, B. J.; Taylor, P. A.; Winton, R. I. *Surf. Sci.* **1979**, *83*, 181.

(17) Broden, G.; Rhodin, T.; Capehart, W. *Surf. Sci.* **1976**, *61*, 143.

Solid-State Bromination of Poly(1,6-di-*N*-carbazolyl-2,4-hexadiyne): A ^{13}C CP-MAS NMR Study

Hellmut Eckert,[†] James P. Yesinowski,[*†] Daniel J. Sandman,[‡] and Christopher S. Velazquez[‡]

Contribution No. 7509 from the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and GTE Laboratories, Incorporated, Waltham, Massachusetts 02254.

Received February 11, 1986.
Revised Manuscript Received September 18, 1986

Abstract: ^{13}C cross-polarization/magic-angle spinning (CP-MAS) NMR experiments at 50.36 MHz reveal that the solid-state reaction of the crystalline polymer poly(*N*-dicarbazolyl-2,4-hexadiyne) (poly-DCH) with liquid bromine results in the formation of covalent C-Br bonds in the polymer. The presence of bromine in these compounds results in loss of the signals arising from those carbon atoms directly bonded to or adjacent to bromine due to broadening effects arising from dipolar coupling to the quadrupolar $^{79,81}Br$ isotopes. Nevertheless, ^{13}C CP-MAS NMR can identify carbon atoms more than two bonds removed from bromine and allows one to monitor semiquantitatively the course of the bromination. By comparison with model compounds it is shown that bromine effects selective electrophilic aromatic substitution at the 3,6 positions on the aromatic rings of the carbazole moiety, forming a polymer with four Br per repeat unit. At higher bromination levels addition to the multiple bonds in the backbone occurs. For the material of composition poly-DCH($Br_{6.0}$), the results indicate extensive conversion of the polydiacetylene structure to a mixed polyacetylene structure. The observation of additional weak absorptions corresponding to butatrienic units suggests that the bromine-backbone interaction leads to localization of conjugation defects.

The homogeneous topochemical polymerization of conjugated diacetylene monomers produces macroscopic polymer single crystals with a high degree of perfection.[1] The polydiacetylenes thus formed (see eq 1) have a fully conjugated planar backbone and are, as wide-band one-dimensional semiconductors, of fundamental theoretical interest from a solid-state physics viewpoint. In addition, they possess optical and electronic properties that are unusual for polymers and which suggest applications in electronic

---

[†] California Institute of Technology.
[‡] GTE Laboratories, Inc.

(1) Enkelmann, V. In *Polydiacetylenes*; Cantow, H.-J.; Ed.; Spinger-Verlag: Berlin, Heidelberg, New York, Tokyo, 1984; p 91.

0002-7863/87/1509-0761$01.50/0