absorption and emission spectra were recently described;[24b] a comparison of the geometrical parameters with those of our oxo carbamato complex shows a close resemblance between the two compounds. The only apparent difference is a slight shortening of the $Zn-O_2CNEt_2$ average distance (1.915 (6) Å) with respect to the $Zn-O_2CMe$ value (1.98 Å). This can be rationalized on the basis of an increased electron density on the diethylcarbamato ligand, with a consequent stronger interaction with the cation.

It is interesting to note that the compound reported in this paper is highly symmetrical, and the diethylcarbamato groups are of one type only, namely bridging bidentate. This is a unique feature within tetranuclear compounds of this category; usually only mononuclear species, such as $Si(O_2CN^iPr_2)_4$[25] or $Hf(O_2CN^iPr_2)_4$,[26] or dinuclear species, such as $Cu_2(O_2CNEt_2)_4{\cdot}2NHEt_2$,[27] have a homogeneous set of ligands, i.e. terminal monodentate (Si), terminal bidentate (Hf), or bridging bidentate (Cu).

In view of this unique structural feature and considering the difficulties encountered[5] in structural assignments by IR spectroscopy for this type of compound, the tetranuclear μ_4-oxo species can be regarded as an IR standard for the absorptions associated with the dialkylcarbamato group between 1600 and 1300 cm^{-1}.

μ-Oxo carbamato complexes are not new, and some examples have already been prepared in these laboratories: $U_4O_2(O_2CNEt_2)_{12}$[28] and $Cu_8O_2(O_2CNPr^i_2)_{12}$.[27] These complexes were obtained in low yields during the preparation of the homoleptic carbamates, and their formation was attributed to the presence of an adventitious hydrolytic process. This was confirmed by the experimental observation that good yields of the μ-oxo products could be obtained when the starting dialkylcarbamato complexes were reacted with the required amount of water.[27]

In our case, the synthesis of the zinc diethylcarbamato complex was repeated several times, and special care was taken to avoid the presence of moisture; however, the yields of the μ-oxo derivative roughly corresponded to those obtained (35% of recrystallized product) under the standard operative conditions. Water was therefore unlikely to be responsible for the presence of the μ-oxo ligand in our zinc compound, and a different explanation had to be found. Some literature data were considered first. Zinc metal and carbon dioxide are known[29] to be in equilibrium with ZnO and CO. Moreover, the most convenient route to the $Zn_4O(O_2CR)_6$ carboxylates is the high-temperature reaction between zinc oxide and the carboxylic acid.[23] These facts suggested that the oxygen in our structure could be derived by an analogous route, but the analysis of the reaction products showed that no CO was formed, and diethylformamide was found instead. The identified products thus justify the stoichiometry of eq 4. Labeling experiments with $^{13}CO_2$ confirmed that the carbonyl carbon atom in the formamide originated from CO_2. It therefore seems safe to conclude that the missing oxygen after formamide formation is released as the μ-oxo ligand in the zinc tetramer (cf. eq 1).

$$4Zn + 7Et_2NH + 7CO_2 \rightarrow Zn_4O(O_2CNEt_2)_6 + Et_2NC(O)H + 3H_2 \quad (4)$$

The formation of diethylformamide and the μ-oxo tetramer is probably a concerted process. The possibility that the formation of the μ_4-oxo is accompanied by evolution of CO, which in a subsequent step forms diethylformamide, is unlikely on the basis of the following experimental evidence: (a) the μ-oxo complex and the formamide were obtained, albeit in low yields, even under atmospheric pressure of CO_2 and at lower temperature (70 °C), i.e. where deoxygenation of CO_2 to CO seems unlikely; (b) the reaction between Zn, CO, and $NHEt_2$ under 100 atm of CO at 200 °C did not yield diethylformamide; (c) if Zn and $NHEt_2$ were allowed to react with a stoichiometric amount of labeled $^{13}CO_2$, but in the presence of a large excess of ^{12}CO, labeled diethylformamide was still formed.

The presence of diethylformamide also indicated that the μ-oxo complex could not simply be formed by thermal decomposition of the homoleptic carbamato complex, by analogy with a possible route from $M(O_2CR)_n$ to $MO(O_2CR)_{n-2}$ and carboxylic anhydride.[23] This would have produced the carbamic anhydride, which would decompose to CO_2 and tetraethylurea, rather than to diethylformamide.

To conclude, we believe that free carbon monoxide is not involved in our reaction and suggest that the μ-oxo atom and the formamide are the result of a yet unclear unique transformation of the carbamato group over the zinc surface. This transformation constitutes, beyond any mechanistic speculation, the first example of a CO_2 deoxygenation with simultaneous formation of a metal-oxygen bond and incorporation of CO into an organic molecule.[30]

Acknowledgment. We are grateful to the Consiglio Nazionale delle Ricerche (CNR, Roma), Progetto Finalizzato Chimica Fine II, for financial support (to F.C.) and to Mrs. L. Faccetti, Enichem Synthesis, Milano, for recording the GC-MS spectra. A.B. wishes to thank the Ente Nazionale Idrocarburi, Roma, for a postdoctoral fellowship at the Scuola Normale Superiore di Pisa. The Commission of the European Communities, Bruxelles, has provided a grant to U.E. under the framework of the Science Programme at the Università di Pisa.

Supplementary Material Available: Complete tables of bond distances, bond angles, and thermal parameters (10 pages); a listing of structure factors (5 pages). Ordering information is given on any current masthead page.

---

(24) (a) Koyama, H.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 112. (b) Kunkely, H.; Vogler, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1204.

(25) Belli Dell'Amico, D.; Calderazzo, F.; Dell'Innocenti, M.; Güldenpfennig, B.; Ianelli, S.; Pelizzi, G. *Gazz. Chim. Ital.* **1990**, *120*, 819.

(26) Calderazzo, F.; Ianelli, S.; Pampaloni, G.; Pelizzi, G.; Sperrle, M. *J. Chem. Soc., Dalton Trans.* **1991**, 693.

(27) Agostinelli, E.; Belli Dell'Amico, D.; Calderazzo, F.; Fiorani, D.; Pelizzi, G. *Gazz. Chim. Ital.* **1988**, *118*, 729.

(28) Calderazzo, F.; Dell'Amico, G.; Pasquali, M.; Perego, G. *Inorg. Chem.* **1978**, *17*, 474.

(29) Maier, C. G.; Ralston, O. C. *J. Am. Chem. Soc.* **1926**, *48*, 364.

(30) A communication reported the formation of dialkylformamides or tetraalkylureas from CO_2 and a secondary amine, in the presence of Pd(II) salts as catalyst,[31] but no mechanistic details are available.

(31) Morimoto, Y.; Fujiwara, Y.; Taniguchi, H.; Hori, Y.; Nagano, Y. *Tetrahedron Lett.* **1986**, *27*, 1809.

Contribution from the Department of Chemistry,
University of Southern California,
Los Angeles, California 90089-0744

Behavior of Phosphoryl Trifluoride toward Dry Trimethylamine Oxide: Complex Formation and Disproportionation, and Action of Lewis Acids

Anton B. Burg

Received January 23, 1991

A recent study of the behavior of $SiCl_4$ and SiF_4 toward dry trimethylamine oxide (hereinafter TMAO)[1] implied the possibility that similar work with $POCl_3$ and POF_3 also would be interesting. For the present study, POF_3 was chosen because steric inhibitions would be minimal and its high volatility would make possible the use of high-vacuum methods to determine combining ratios at low temperatures; also, NMR spectra would aid interpretation. One exploratory experiment did show interesting results for $POCl_3$, but it was not feasible to prove the detailed chemistry by NMR spectra.

It was found to be easy enough to demonstrate clean formation of the 1:1 complex $TMAO{\cdot}POF_3$ at temperatures in the −80 °C region. This complex, warmed rapidly to 25 °C and then finally to 50 °C for removal of all volatiles, decomposed to give PF_6^- and

---

(1) Burg, A. B. *Inorg. Chem.* **1989**, *28*, 3608.

0020-1669/91/1330-3781$02.50/0

a product including the PF_2^+ unit.

In this TMAO complex, the attachment of TMAO to P improved the base action of the P=O part; then HCl was held sufficiently strongly not to be directly recoverable as such. Instead, POF_3 was slowly released at −78 °C, leaving TMAO·HCl. Or, on sudden heating to 25 °C, there was considerable formation of PF_6^-, PF_2^+, and even some product containing the PF unit, with liberation of some HCl but retention of all TMAO.

The strong bonding of HCl in the complex $TMAO{\cdot}POF_3{\cdot}HCl$ shows that bonding of TMAO to P enhances the base action of the P=O unit; without TMAO, POF_3 fails to hold HCl. For the same reason, the 1:1:1 complex $TMAO{\cdot}POF_3{\cdot}BF_3$ can be formed cleanly at low temperatures, with no observable dissociation pressure like that of $POF_3{\cdot}BF_3$ at −78 °C (near 6 mm). In this case also, it is possible to show some formation of PF_6^- and PF_2^+ units by fast heating of the 1:1:1 complex, but apparently much less than in the HCl case, and no PF unit could be demonstrated.

Experimental Methods

The modified Stock-type high-vacuum methods used here have been described in earlier publications.[2] As before, the NMR δ values are in ppm, upfield of the standard (but downfield for protons) and the symbol ${}_nJ$ (s^{-1}) indicates multiplicity.

POF_3 was made from PF_3 by action of NO_2, with removal of NO_2, NO, and N_2O in the high-vacuum line. PF_3 had been made from PCl_3 and SbF_3 in a Pyrex glass tube; then the expected impurities SiF_4 and BF_3 were removed as their known complexes with $(CH_3)_3N$. The ^{31}P NMR spectrum of the liquid in a sealed tube at 13 atm ($\delta = 33.3$ ppm from H_3PO_4; ${}_4J = 1038$) showed no more than 1% phosphorus impurity. The ^{19}F spectrum showed $\delta = 92.3$ ppm (from Cl_3CF), with ${}_2J = 1059$—a high value not clearly explained. The identification of PF_6^- by its ^{31}P septet was confirmed by comparison with KPF_6 ($\delta = 150$, with ${}_7J = 709$) in solution in D_2O.

Specific Procedures, Results, and Discussion

Action of PF_3 on TMAO. The study actually began with an attempt to form the adduct $TMAO{\cdot}PF_3$. PF_3 (0.269 mmol) was brought into contact with a chloroform solution of TMAO (0.810 mmol) at −60 °C. Then the volatiles were treated with a known amount of HCl to prove the presence of 0.243 mmol of $(CH_3)_3N$; and 0.025 mmol of POF_3 was isolated as such. From the solid residue, 0.323 mmol of TMAO was recovered by high-vacuum sublimation. Thus the amount of consumed TMAO was 0.487 mmol, and the yield of P in nonvolatile form, 0.244 mmol. This 2:1 ratio corresponds to the equations

$$\mathrm{TMAO} + \mathrm{PF_3} \rightarrow \mathrm{TMA} + \mathrm{POF_3} \qquad (1)$$

$$\mathrm{TMAO} + \mathrm{POF_3} \rightarrow \mathrm{TMAO{\cdot}POF_3} \qquad (2)$$

Actually, the presumed 1:1 adduct proved to be very unstable; hence its actual existence at low temperatures was not certain until its attachment of HCl or BF_3 was studied later.

Decomposition of the Apparent 1:1 Adduct. An experiment involving 0.522 mmol of POF_3 and 0.398 mmol of solid TMAO, at temperatures as high as 50 °C, led to an apparent combining ratio of 0.97 POF_3 per TMAO; however, the solid product was not $TMAO{\cdot}POF_3$, but decomposition products demonstrable by NMR spectra. With the product suspended in acetone-d_6, the ^{31}P spectrum showed PF_6^- at $\delta = 143$ (${}_7J = 708$) and a substance containing the PF_2 unit at $\delta = 16$ (${}_3J = 953$). In the ^{19}F spectrum, PF_6^- appeared at $\delta = 71$ (${}_2J = 708$) and PF_2 at $\delta = 82$ (${}_2J = 953$). The relative intensities showed a 7:2 ratio of PF_2 to PF_6^-. Not understood were a ^{19}F doublet of doublets at $\delta = 59$ (${}_2J = 747$ and 56) and another (twice as intense) at $\delta = 60$ (${}_2J = 774$ and 52); not seen in the ^{31}P spectrum, they may have represented destruction of some TMAO, or possibly P-containing polymers with ^{31}P peaks so broad as not to rise above the noise level. There was no ^{31}P or ^{19}F doublet for PF, which was found in later experiments.

In a more delicately controlled experiment, the 1:1 adduct was precipitated from H_2CCl_2 at −78 °C and suspended in acetone-d_6 at 25 °C. The ^{31}P NMR spectrum showed the PF_2 unit at $\delta = 16.9$ (${}_3J = 941$) and PF_6^- at $\delta = 143$ (${}_7J = 707$). Again, there was no doublet.

The 1:1 Adduct with HCl. If, as expected, the bonding of TMAO to POF_3 through the PF_3 triangle would enhance the bonding power of O in the PO unit, one result might be the stabilization of the $TMAO{\cdot}POF_3$ complex as the HCl adduct $TMAO{\cdot}POF_3{\cdot}HCl$. Indeed, when 0.771 mmol of $TMAO{\cdot}POF_3$ (formed quantitatively by precipitation from H_2CCl_2 during $^1/_2$ h at −87 °C) was exposed to HCl in excess, the amount of absorbed HCl was accurately in agreement with the formula $TMAO{\cdot}POF_3{\cdot}HCl$, with no observable dissociation pressure at −78 °C. Then during 19 h at −78 °C this 1:1:1 complex liberated all of the POF_3, proving that this had been present as such in the 1:1:1 complex.

However, a second experiment showed that the 1:1:1 complex could undergo partial disproportionation by sudden heating in vacuo to 25 °C. The sample had been made from 1.145 mmol of TMAO, 1.104 mmol of POF_3, and 1.153 mmol of HCl, first precipitating the 1:1 complex from H_2CCl_2 at −78 °C and then adding the HCl at that temperature. As the volatiles were removed to the vacuum line during fast heating to 25 °C, the hard, lumpy product burst into fragments easily transferable to an NMR tube.

The recovery of POF_3 from this experiment was 0.870 mmol (79%); presumably a like amount of TMAO·HCl had been formed. Then the rest of the POF_3 had undergone disproportionation. The ^{31}P NMR spectrum (solid product suspended in acetone-d_6) again showed this reaction: the triplet for PF_2 was at $\delta = 15.5$, with ${}_3J = 964$; and the septet for PF_6^- was at $\delta = 143$, with ${}_7J = 710$. But now there was a doublet at $\delta = 7.2$, with ${}_2J = 929$, clearly due to an entity including the PF unit. The ^{19}F spectrum confirmed these: PF_6^- was at $\delta = 71.8$, with ${}_2J = 708$; PF_2 was at $\delta = 82.2$, with ${}_2J = 953$; and PF was at $\delta = 74.1$, with ${}_2J = 929$. The ^{19}F NMR spectrum showed the relative intensities for PF_6^-:PF_2:PF as 45:125:10; then the corresponding ratio for P units was 3:25:4. However, the meaning of this ratio is not quite clear, for it may represent only what was soluble in acetone; the contribution of the insoluble solid cannot be judged. In most other disproportionation experiments, the ratio of PF_2 to PF_6^- was closer to 4.

Boron Trifluoride with Phosphoryl Trifluoride. The very weak combination of POF_3 with BF_3 was demonstrated by an experiment in which 0.683 mmol of POF_3 and 0.785 mmol of BF_3 were mixed well in the gas phase and cooled to −110 °C. Then it was possible at that temperature to draw off into the vacuum line only 0.098 mmol of BF_3, proving the formula $POF_3{\cdot}1.006BF_3$ for the white solid residue. The dissociation pressures of this adduct were measured as 6.4 mm at −78.5 °C, 14.3 mm at −71.3 °C, 37.0 mm at −62.8 °C, and 144 mm at −49.0 °C; hence $\log P = 11.148 - 2015/T$. In the vapor phase, dissociation was complete.

The 1:1:1 Adduct with Boron Trifluoride. As expected, the attachment of TMAO to POF_3 led to firmer bonding of BF_3 to P–O. The resulting 1:1:1 adduct showed no dissociation pressure at −78 °C, whereas $POF_3{\cdot}BF_3$ shows nearly 7 mm pressure at that temperature. Indeed, rather than direct dissociation, this adduct at −78 °C slowly liberates POF_3 to form $TMAO{\cdot}BF_3$; instead of coming off itself, BF_3 displaces POF_3. After precipitation from H_2CCl_2 at −97 °C, $TMAO{\cdot}POF_3$ was treated with equimolar BF_3, virtually all of which was absorbed. Then during 17 h at −78 °C, just 100% of the POF_3 was delivered to the high-vacuum line and isolated.

In all experiments in which there was fast warming of $TMAO{\cdot}POF_3{\cdot}BF_3$ to 25 °C, the displacement process was strongly dominant, but traces of PF_6^- and PF_2 units were found by their NMR spectra; it appeared that the disproportionation amounted to considerably less than in the case of $TMAO{\cdot}POF_3{\cdot}HCl$. Here again, there was no intelligible side reactions.

TMAO with $POCl_3$. One experiment was enough to confirm that POF_3 is better than $POCl_3$ for meaningful work with TMAO. TMAO (0.966 mmol, dissolved in H_2CCl_2) was treated with 0.919 mmol of $POCl_3$ during warming from −78 to +25 °C. The solvent was drawn off to the vacuum line at −45 °C, and then it was possible to isolate 0.531 mmol of $POCl_3$. Thus the white solid

---

[2] Burg, A. B. *Inorg. Chem.* **1989**, *28*, 1295.

product had the empirical formula $POCl_3 \cdot 2.5TMAO$. This compares with $SiCl_4 \cdot 3.3TMAO$, formed under similar conditions.[1] Then heating under vacuum brought the formula to $POCl_3 \cdot 1.68TMAO$ for the hard, brown residue. Very little of this dissolved in D_2O, giving only singlets for the ^{31}P NMR spectrum. The smallest of these (at $\delta = -0.6$ ppm) showed slight hydrolysis to D_3PO_4. Other small singlets at $\delta = 10.9$, 11.4, 21.0, and 38 ppm would not be P–F compounds—possibly impurities. The major feature was a broad singlet at $\delta = 24$ ppm, for the suspended solid, the P–Cl content of which evidently was protected against hydrolysis.

Rationale. The disproportionation of POF_3 as it is being liberated from one of the 1:1:1 complexes might begin with processes conjectured as

$$4POF_3 \rightarrow PF_6^- + 3POF_2^+ + O^{2-} \qquad (3)$$

$$2POF_2^+ \rightarrow POF_3 + POF^{2+} \qquad (4)$$

$$POF^{2+} + O^{2-} \rightarrow PO_2F \qquad (5)$$

wherein (4) and (5) would be highly variable. When the PF unit is not seen in the NMR spectra, its P–F coupling might be lost in the breadth of the polymer peak; for PO_2F must be polymeric. Also, there may be other ways to employ O^{2-}.

Since PCl_6^- is far less stable than PF_6^-, $POCl_3$ cannot be expected to behave in the manner of (3). Instead, it would be reasonble to expect $POCl_3$ to react with TMAO more in the manner of its nearly isoelectronic analogue $SiCl_4$, as indeed it does.

Significance. We find here some analogy to prior reports of the disproportionation of POF_3 by various sources of the F^- ion. Lustig and Ruff[3] found that the low lattice energy of CsF makes F^- sufficiently available for an attack on POF_3 to make PF_6^- and $PF_2O_2^-$; and also of interest is the action of KF on $PSCl_3$ to form KCl, KPF_6, and KPF_2S_2. The present work shows that TMAO has enough electron-donor bonding power to displace F^- and even O^{2-} from POF_3, for action of these on other P sites; but it does not yet seem possible to determine just how many TMAO molecules form stabilizing attachments to O–P–F units.

The chemical versatility of TMAO is further demonstrated by other effects such as the oxidation of PF_3 to form POF_3 and the removal of HCl or BF_3 from the 1:1:1 complexes, for recovery of POF_3 as such. Indeed, the actual existence of the 1:1:1 complexes demonstrates the ability of TMAO to increase the electron-donor bonding power of a molecule to which it makes a dative bond.

---

(3) Lustig, M.; Ruff, J. K. *Inorg. Chem.* **1967**, *6*, 2115.

Contribution from the Institut für Anorganische
Chemie der Universität, Auf der Morgenstelle 18,
D-7400 Tübingen 1, West Germany

^{31}P and ^{29}Si Solid-State NMR Studies of a Phosphine-Functionalized Polysiloxane Framework

Ekkehard Lindner,* Armin Bader, and Hermann A. Mayer

Received August 27, 1990

Over the past few years, there has been an increasing interest in the preparation of immobilized homogeneous catalysts,[1-3] in chromatography,[4,5] and in fundamental studies in the field of surface chemistry.[6] These developments have spurred the synthesis of polymer-supported ligands and organometallic compounds. To that end, a great variety of organic resins and inorganic oxides have been used as base matrices. Among the latter class of supports, silica has gained outstanding importance due to its rigid structure and the ease of functionalization through its surface silanol groups.[7] However, phosphinated silicas obtained by treating even highly dispersed SiO_2 with reactive (chlorosilyl)alkylphosphines or (methoxysilyl)alkylphosphines suffer from great disadvantages, namely low ligand content and low surface loading. In order to overcome this drawback, phosphine-modified polysiloxane frameworks have been prepared by hydrolysis of (trimethoxysilyl)alkylphosphines ("sol–gel process").[8-12] Their cocondensation with x mol of tetraethoxysilane leads to solid polymers of the approximate stoichiometry $[SiO_{3/2}(CH_2)_nPR_2] \cdot xSiO_2$. Thus, a wide range of ligand densities may be realized. Such a "surface tailoring" is novel and represents a most promising technique for the preparation of supported organometallic species. It also opens up the possibility of studying their behavior as a function of the ligand density. Despite the preparative work that has been undertaken,[8-12] there is still a lack of detailed structural information. In this work, we present ^{31}P and ^{29}Si CP-MAS data for $[SiO_{3/2}(CH_2)_6P(Ph)CH_2CH_2OCH_3] \cdot 2SiO_2$ (**1**),[13] which contains a potentially bidentate ligand with oxygen and phosphorus donor atoms. This type of ligand has recently found outstanding applications in coordination chemistry and catalysis.[14] Cross-polarization magic-angle-spinning (CP-MAS) solid-state NMR spectroscopy is a powerful tool for the investigation of insoluble systems of this kind.[15-18]

Experimental Section

All manipulations were performed under argon by employing the usual Schlenk techniques. Ethanol was dried with sodium and stored under argon. The elemental analyses were carried out on a Carlo Erba analyzer, Model 1106. IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. The CP-MAS solid-state NMR spectra were recorded on a Bruker MSL 200 multinuclear spectrometer with a wide-bore magnet (4.7 T) using samples of 200–300 mg in double-bearing rotors of ZrO_2. MAS was performed at a 4-kHz spinning rate. Frequencies and standards: ^{31}P, 81 MHz ($NH_4H_2PO_4$); ^{29}Si, 39.75 MHz (Q_8M_8[19]); recycle delay, 2 s. T_{SiH}, $T_{1\rho H}$ and I_0 values were calculated by using the Bruker software SIMFIT.

Reagents. $Si(OEt)_4$ and $(n\text{-}Bu)_2Sn(OAc)_2$ (Merck) were of analytical grade and were used without further purification. The ether–phosphine ligand $(MeO)_3Si(CH_2)_6P(Ph)CH_2CH_2OCH_3$ (**2**) was obtained according to a previously published procedure.[7]

Preparation of Ligand 1. Ethanol was added dropwise to a mixture of **2** (1.921 g, 5.16 mmol), $Si(OEt)_4$ (2.148 g, 10.31 mmol), and water (0.511 g, 28.36 mmol) until a homogeneous solution was formed. After addition of the catalyst $(n\text{-}Bu)_2Sn(OAc)_2$ (0.2 g) and stirring of the reaction medium for 24 h, the white precipitate was isolated and washed with ethanol and dichloromethane (three times each, 10 mL). Yield: 1.60 g (75%). IR: $\nu_{as}(SiO_2)$ 1100–1050 cm^{-1}. Anal. Calcd. for the idealized stoichiometry $[SiO_{3/2}(CH_2)_6P(Ph)CH_2CH_2OCH_3] \cdot 2SiO_2$: C,

---

(1) Pittman, C. U. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Chapter 55, p 553.

(2) Hartley, F. R. *Supported Metal Complexes*; D. Reidel Publishing Co.: Dordrecht, The Netherlands 1985.

(3) Lindner, E.; Bader, A.; Glaser, E.; Wegner, P. *J. Mol. Catal.* **1989**, *56*, 86.

(4) Pfleiderer, B.; Albert, K.; Bayer, E. *J. Chromatogr.* **1990**, *506*, 343.

(5) Bayer, E.; Albert, K.; Reiners, J.; Nieder, M.; Müller, D. *J. Chromatogr.* **1983**, *264*, 197.

(6) Lamb, H. H.; Gates, B. C.; Knözinger, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1127.

(7) Lindner, E.; Bader, A.; Glaser, E.; Pfleiderer, B.; Schumann, W.; Bayer, E. *J. Organomet. Chem.* **1988**, *355*, 45.

(8) Schubert, U.; Egger, C.; Rose, K.; Alt, C. *J. Mol. Catal.* **1989**, *55*, 330.

(9) Khatib, I. S.; Parish, R. V. *J. Organomet. Chem.* **1989**, *369*, 9.

(10) Parish, R. V.; Habibi, D.; Mohammadi, V. *J. Organomet. Chem.* **1989**, *369*, 17.

(11) Deschler, U.; Kleinschmit, P.; Panster, P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 236.

(12) Kavan, V.; Čapka, M. *Collect. Czech. Chem. Commun.* **1980**, *45*, 2100.

(13) Lindner, E.; Bader, A.; Mayer, H. A. *Z. Anorg. Allg. Chem.*, in press.

(14) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27.

(15) Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 7606.

(16) Pfleiderer, B.; Albert, K.; Bayer, E.; van de Ven, L.; de Haan, J.; Cramers, C. *J. Phys. Chem.* **1990**, *94*, 4189.

(17) Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J. *J. Phys. Chem.* **1985**, *89*, 277.

(18) Harris, R. K. *Analyst* **1985**, *110*, 649.

(19) Lippmaa, E.; Samoson, A. *Bruker Rep.* **1982**, *1*, 6.

0020-1669/91/1330-3783$02.50/0