

Reactivity of Surface Intermediates Derived from Al₂O₃-Supported Ru₃(CO)₁₂ in the CO + H₂ Reaction

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The effect of subcarbonyl surface intermediates resulting from Ru₃(CO)₁₂ molecular clusters supported on Al₂O₃ in the CO hydrogenation has been investigated by using an isotope-labeling technique. It has been established that single ruthenium atoms are stabilized in the form of dicarbonyl species, characterized by 2072- and 2001-cm⁻¹ IR frequencies, when temperature-programmed decomposition (TPDE) is carried out in the temperature range between 473 and 573 K. Despite the presence of Ru^{II}(CO)₂, free ruthenium sites are responsible for the catalytic activity in the ¹³CO hydrogenation reaction. The high mobility of the CO ligands in the surface ruthenium dicarbonyl species, demonstrated by CO molecular exchange during the reaction, makes the CO from the dicarbonyl species compete successfully with that chemisorbed from the gas phase labeled in the form of ¹³CO. An explanation for the stability of the highly dispersed ruthenium particles and detailed mechanisms of the surface reactions are given.

1. Introduction

Metal dispersion of the Ru/Al₂O₃ catalysts derived from the Ru₃(CO)₁₂ carbonyl cluster proved to be higher than for those prepared by an incipient wetness method.¹⁻³ Further studies demonstrated that thermal decomposition plays an important role in the formation of active sites; e.g. decomposition in helium yields species of higher activity than decomposition in hydrogen.⁴⁻⁶ Generally, when decomposition is performed up to 570 K, a catalyst is produced that is more active than that heated to 770 K.⁷ This higher activity might be attributed to the presence of dicarbonyl species, as was demonstrated by IR techniques.⁸ This assumption is also supported by other studies. Earlier it was established that Os(II)-dicarbonyl species derived from osmium clusters are the active sites in the CO + H₂ reaction.⁹ It was also found that, during decomposition in a mild, nonreductive atmosphere, the cluster framework breaks up and triosmium ensembles are formed whereas under a hydrogen atmosphere, at higher temperature, osmium aggregates are the prevailing species on the support.¹⁰ The triosmium ensembles proved to be stable under the CO hydrogenation conditions, most likely due to the presence of CO ligands.¹¹ For the formation of methane and oxygenates metal aggregates and a mononuclear osmium complex, respectively, were suggested as active sites.

The inactivity of the triruthenium species was also demonstrated in the Ru₃(CO)₁₂/Cab-O-Sil system with use of IR techniques.⁶ However, on an alumina support monoruthenium dicarbonyl species were already apparent after impregnation, and this was ascribed to a more extensive interaction between the cluster framework and the alumina support.¹²⁻¹⁶

Table I. Quantitative Evaluation of the TPDE Experiments for Ru₃(CO)₁₂/Al₂O₃ Samples

solvent	TPDE, K	amt of CO, μmol (g of catalyst) ⁻¹				total
		initial	decomposed			
			T < 473 K	473 < T < 573 K	T > 573 K	
pentane	770	792	295	198	195	688 ^a (87%)

^a Correction is made for the hydrocarbon moieties evolved with CO and determined by FID.

Dicarbonyl species on the catalyst prepared from Ru₃(CO)₁₂ supported on alumina and characterized by bands at 2040 and 1960 cm⁻¹ were also observed by Kellner and Bell.¹⁷ However, these bands were shown to be quite stable and the prevailing band of CO during the reaction at higher pressure was observed at 2010 cm⁻¹; this was assigned to a monocarbonyl species. The conclusion from these experiments was that monocarbonyl species chemisorbed on ruthenium metallic sites are the active intermediates during CO hydrogenation.

It is well-known that in CO hydrogenation to form hydrocarbons over metal surfaces CO is dissociated on metallic sites.¹⁸ On these sites the dissociation is preceded by CO chemisorption that is believed to be in linear form as indicated by Kellner and Bell.¹⁷ However, the question to be answered is why the metallic sites become more active when dicarbonyl species are present on the surface.

The main goal of the present work is to investigate the formation and the reactivity of the Ru metallic sites and the Ru(CO)₂ species formed during the decomposition of Ru₃(CO)₁₂. In order to distinguish between the CO species remaining on the surface and those chemisorbed from the gas phase, a ¹³C-labeling technique was used along with CO chemisorption to determine the free metallic surface and infrared spectroscopy to study the transformation of the surface dicarbonyl species.

2. Experimental Section

2.1. Materials. Ru₃(CO)₁₂ to an extent of 2 wt % metal was deposited on an alumina (Degussa ALON C) surface from pentane solution as described earlier.¹⁹ Prior to impregnation Al₂O₃ was partially dehydroxylated. All gases were carefully purified by using a manganese deoxygenation unit and a 13X molecular sieve trap. The isotopically labeled CO gas was enriched with ¹³C to a level of 98%.

2.2. Apparatus and Procedure. Temperature-programmed decomposition (TPDE) of the supported cluster was carried out under helium, and

- Guzzi, L.; Matusek, K.; Manninger, I.; Király, M.; Eszterle, M. *Preparation of Catalysts*; Elsevier: Amsterdam, 1979; Vol. II, p 391.
- Guzzi, L.; Schay, Z.; Matusek, K.; Bogay, I.; Stefler, G. *Proceedings of the 7th International Congress on Catalysis*; Elsevier: Amsterdam, 1981; p 211.
- Guzzi, L.; Schay, Z.; Bogay, I. *Preparation of Catalysts*; Elsevier: Amsterdam, 1983; Vol. III, p 451.
- Schay, Z.; Guzzi, L. *Acta Chim. Hung.* **1982**, *111*, 607.
- Lázár, K.; Schay, Z.; Guzzi, L. *J. Mol. Catal.* **1982**, *17*, 205.
- Schay, Z.; Lázár, K.; Mink, J.; Guzzi, L. *J. Catal.* **1984**, *87*, 179.
- Böszörményi, I.; Dobos, S.; Guzzi, L.; Markó, L.; Lázár, K.; Reiff, W. M.; Schay, Z.; Takács, L.; Vizi-Orosz, A. *Proceedings of the 8th International Congress on Catalysis*; Chemie Verlag: Weinheim, FRG, 1984; Vol. 5, p 183.
- Guzzi, L.; Dobos, S. *Homogeneous and Heterogeneous Catalysis*; VNU Science: Utrecht, The Netherlands, 1986; p 901.
- Knözinger, H.; Zhao, Y.; Barth, R.; Epstein, R.; Gates, B. C.; Scott, J. P. *Faraday Discuss. Chem. Soc.* **1981**, *72*, 53.
- Schwank, J.; Allard, L. F.; Decba, M.; Gates, B. C. *J. Catal.* **1983**, *84*, 27.
- Odeunmi, E. O.; Matrana, B. A.; Datye, A. K.; Allard, L. F.; Schwank, J.; Manogue, W. H.; Hayman, A.; Onuferko, J. H.; Knözinger, H.; Gates, B. C. *J. Catal.* **1985**, *95*, 370.
- Guglielminotti, E.; Zecchina, A.; Bossi, A.; Camia, M. *J. Catal.* **1982**, *74*, 252.
- Dobos, S.; Böszörményi, I.; Silberer, V.; Guzzi, L.; Mink, J. *Inorg. Chim. Acta* **1985**, *96*, L13.

- Dobos, S.; Böszörményi, I.; Mink, J.; Guzzi, L. *Inorg. Chim. Acta* **1986**, *120*, 135.
- Dobos, S.; Böszörményi, I.; Mink, J.; Guzzi, L. *Inorg. Chim. Acta* **1986**, *120*, 145.
- Kuznetsov, V. L.; Bell, A. T.; Yermakov, Yu. I. *J. Catal.* **1980**, *65*, 374.
- Kellner, C. S.; Bell, A. T. *J. Catal.* **1982**, *75*, 251.
- Ponec, V. *Coal Sci.* **1984**, *3*, 1.
- Lázár, K.; Matusek, K.; Mink, J.; Dobos, S.; Guzzi, L.; Vizi-Orosz, A.; Markó, L.; Reiff, W. M. *J. Catal.* **1984**, *87*, 163.

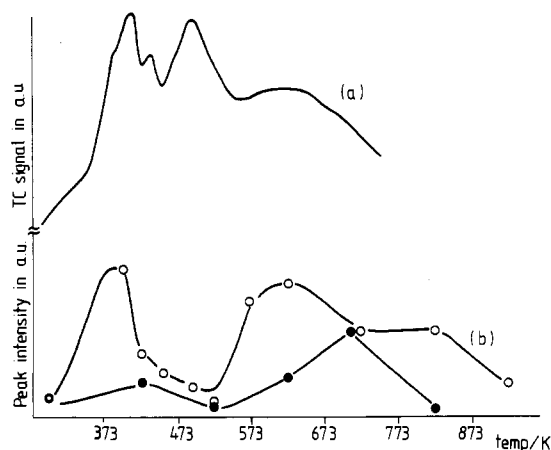


Figure 1. (a) Temperature-programmed decomposition (TPDE) for Ru₃(CO)₁₂ and (b) TPDE-MS analysis for CO and CO₂: (○) CO; (●) CO₂.

the gases evolved were monitored simultaneously by FID and TC detectors. In some cases the effluent gas after the TC detector was analyzed by mass spectrometry at *m/e* 15, 28, and 44, for CH₄, CO, and CO₂, respectively.

CO chemisorption was measured at room temperature in a pulse system. Separate samples were heated to the required temperature under He and then cooled down to room temperature, and CO chemisorption was started.

A Fourier transform infrared spectrometer (DIGILAB FTS-20C) was used *ex situ* to measure the type and quantity of the CO left on the surface after the different procedures. The catalytic activity of the samples was measured in a tubular flow reactor using a 3:1 H₂/CO mixture with a flow rate of 15 mL min⁻¹. The ¹³C-labeling experiments were performed in an all-glass circulating reactor using a 5:1 H₂/CO mixture. The reactant and the products were analyzed by means of a Packard Type 427 gas chromatograph equipped with a Porapak Q column. After separation the quantity was determined by FID (CO and CO₂ were first converted into methane). The isotope content was measured by mass spectrometry with a Du Pont 21-490/B single-focusing instrument interfaced to the gas chromatograph.

3. Results

3.1. Determination of the Surface Species. Before any catalytic reaction, the amount and the structure of the subcarbonyl species must be clarified. The TPDE pattern of Ru₃(CO)₁₂ on alumina under He presented in Figure 1 is very similar to that obtained earlier.² In the lower part of Figure 1 the gas analysis indicates that between 473 and 573 K there is a minimum in CO evolution. The main peak in this region represents hydrocarbons, mainly methane, which partly results from the pentane remaining on the alumina after impregnation.

From the TPDE results the number of CO ligands retained on the subcarbonyl species in the temperature range mentioned can be estimated as shown in Table I.

The structure of the CO ligands present in the subcarbonyl species in the temperature range between 473 and 573 K was studied by IR techniques. In Figure 2 the spectra of the impregnated cluster (Figure 2a) as well as of material decomposed at different temperatures (Figure 2b–f) are presented. The spectrum of the impregnated sample was taken immediately after the solvent removal. Some bands characteristic of the original cluster (at 2062 and 2032 cm⁻¹) were still present, but bands that could be assigned to Ru^{II}(CO)₂ species formed from the decomposed cluster were already visible (2072 sh, 2001 s cm⁻¹).^{2,13} In the range between 473 and 573 K, the intensities of these two prevailing bands decreased and disappeared above about 573 K. Simultaneously, with increasing temperature a single band developed at 1872 cm⁻¹ but also disappeared above 573 K.

During thermal decomposition when partial removal of CO ligands and reconstruction of the metal framework occur, free ruthenium sites are also created. The amount of these surface sites can be estimated by room-temperature CO chemisorption. Chemisorption starts when TPDE is carried out up to a little below 473 K as indicated in Figure 3. The CO uptake on the sample,

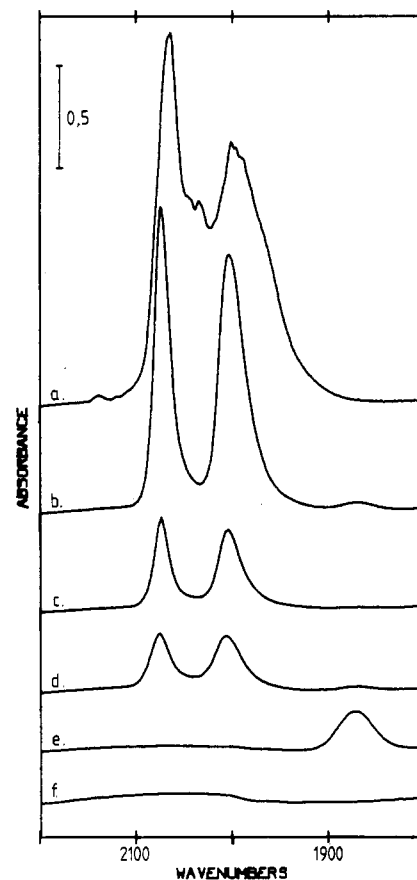


Figure 2. IR spectra for Ru₃(CO)₁₂/Al₂O₃ during TPDE under He: (a) after impregnation; (b) at 473 K for 30 min; (c) at 493 K for 30 min; (d) at 523 K for 30 min; (e) at 573 K for 30 min; (f) at 773 K for 30 min.

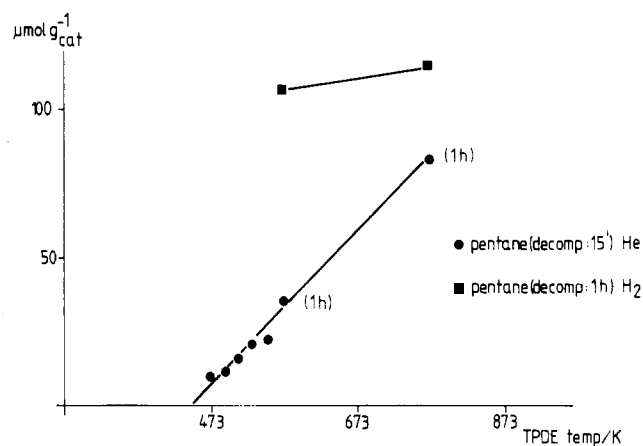


Figure 3. CO chemisorption at room temperature after TPDE up to the temperature indicated at the abscissa: (●) decomposition under He for 15 min; (■) decomposition under H₂ for 1 h.

decomposed up to the indicated temperature and held isothermally for 15 min, linearly increases with the TPDE temperature. An enhancement in the amount of the CO chemisorbed could be observed when the hold-on time was increased or the temperature and the atmosphere of TPDE (He to H₂) were changed.

The mode of CO chemisorption after full decomposition of Ru₃(CO)₁₂ was measured by the IR technique and is presented in Figure 4. The room-temperature reabsorption of CO shows a three-band structure (2141, 2075, and 2017 cm⁻¹) in agreement with that determined in the Ru₃(CO)₁₂/Cab-O-Sil system⁶ but not with that obtained over a well-reduced Ru/Al₂O₃ sample.^{20,21}

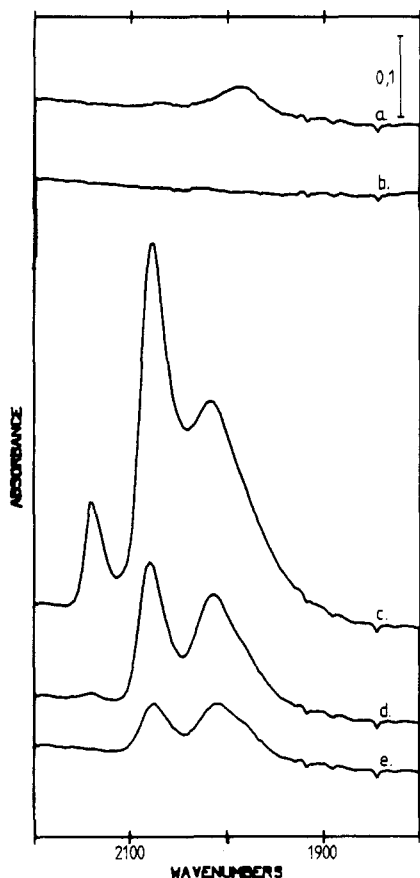


Figure 4. IR spectra of the CO chemisorbed at room temperature: (a) after decomposition in vacuo at 723 K; (b) after hydrogenation at 673 K; (c) after CO chemisorption at room temperature; (d) with heating up to 473 K after chemisorption; (e) with heating up to 573 K after chemisorption.

Table II. Initial Rates of ^{13}CO Exchanges

T , °C	k_1 , mol % s^{-1} (g of catalyst) $^{-1}$	k_2 , mol % s^{-1} (g of catalyst) $^{-1}$	k_1/k_2
194	2.5×10^{-2}	3.8×10^{-3}	6.8
200	2.3×10^{-2}	1.07×10^{-2}	2.2
220	2.4×10^{-2}	1.5×10^{-2}	1.6

In the present system these bands can be assigned to a combination of $\text{Ru}^{\text{III}}(\text{CO})_2$ (2138 and 2070 cm^{-1}) and $\text{Ru}^{\text{II}}(\text{CO})_2$ (2070 and 2005 cm^{-1}),¹³ for which the chemisorption bond strength on Ru (III) species is considerably weaker; thus, this band pair disappears after heating the sample to 473 K.

3.2. Reactivity of $\text{Ru}(\text{CO})_2$ Species and Metallic Ru Sites. As previously indicated, in the temperature range between 473 and 573 K both metallic sites and ruthenium dicarbonyl species are present. In order to distinguish between the reaction pathways utilizing free ruthenium sites and $\text{Ru}(\text{CO})_2$, the catalytic reaction was carried out with a 5:1 $\text{H}_2/^{13}\text{CO}$ mixture.

First it was established that the rate of methanation on a sample, which had been heated to 473 K, was well below 1×10^{-9} mol s^{-1} (g of catalyst) $^{-1}$ at this temperature. The only reaction that could be measured under this condition was molecular isotope exchange between CO ligands in $\text{Ru}(\text{CO})_2$ and ^{13}CO in the gas phase. It is shown in Figure 5. The exchange process can be decomposed into a fast initial part followed by a much slower exchange. The kinetic curve shown in Figure 5 can be approximated by a sum of two exponential rate equations,²² and the calculated initial rates designated by k_1 and k_2 are presented in Table II. One of the exchange reactions is independent of tem-

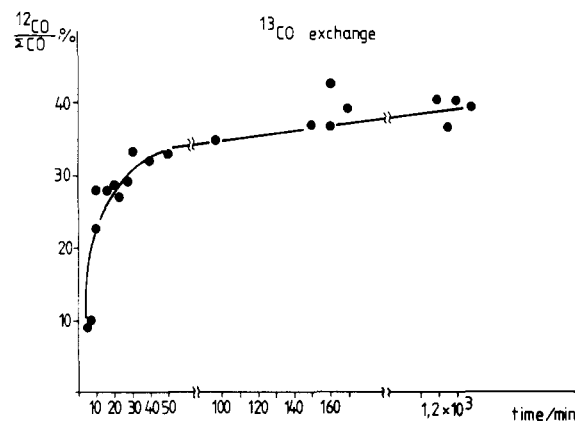


Figure 5. Exchange of gaseous ^{13}CO with ^{12}CO in ruthenium dicarbonyl species at 473 K vs time: TPDE up to 473 K.

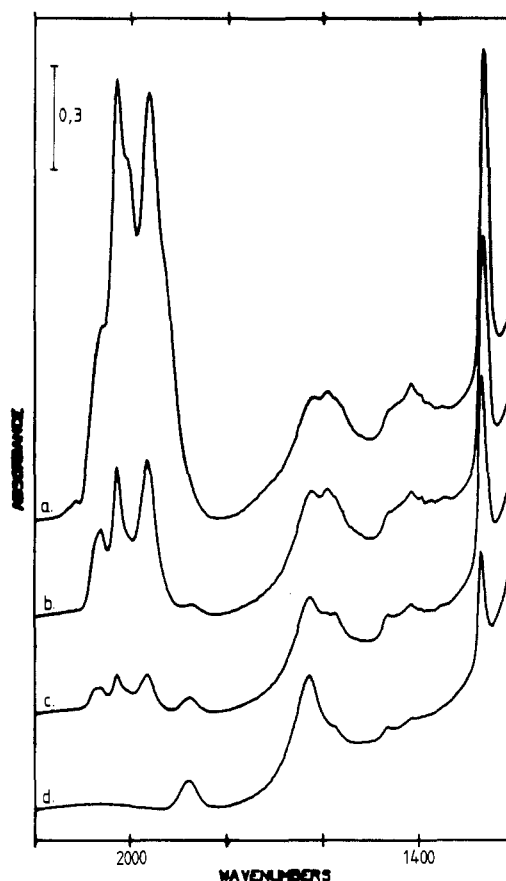


Figure 6. IR spectra of the ^{13}C -substituted dicarbonyl species: (a) at 473 K; (b) at 493 K; (c) at 523 K; (d) at 573 K.

perature whereas the other is strongly temperature-dependent.

Repeated exchange between gaseous ^{13}CO and surface ^{12}CO species results in a change of the two-band IR spectra of the $\text{Ru}^{\text{II}}(\text{CO})_2$ species. As shown in Figure 6, isotope substitution yields another band pair at 2025 and 1958 cm^{-1} , which can be assigned to the exchanged $\text{Ru}^{\text{II}}(\text{CO})_2$ species.

However, the band that appears at 1878 cm^{-1} at higher temperature is not affected by isotope substitution. In Figure 6 the frequency range between 1200 and 1600 cm^{-1} is also presented. The bands here could be assigned to surface carboxylate and hydroxy-carboxylate species,^{23,24} which can most likely be ascribed to a reaction between the CO_2 formed from CO ligands and the alumina support.

(21) Xienxian, G.; Qin, X.; Yongxue, L.; Dai, J.; Pinliang, Y. *Proceedings of the 8th International Congress on Catalysis*; Verlag Chemie: Weinheim, FRG, 1984; Vol. 4, p 599.

(22) Böszörményi, I.; Gucci, L. *Inorg. Chim. Acta* **1986**, *112*, 5.

(23) Little, L. H.; Amberg, C. H. *Can. J. Chem.* **1962**, *40*, 1997.

(24) Yakerson, V. I.; Lafer, L. I.; Danyushevskii, V. Y.; Rubenstein, A. M. *Izv. Akad. Nauk USSR, Ser. Khim.* **1969**, 19.

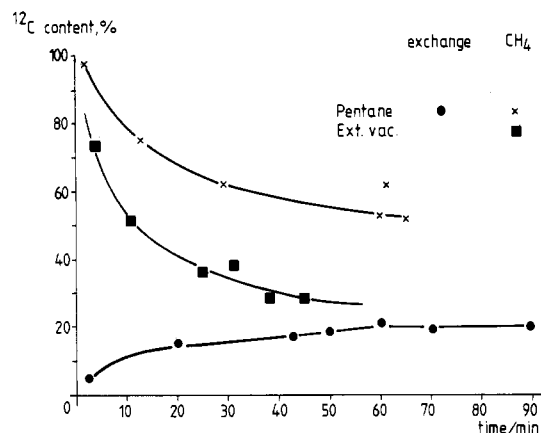


Figure 7. ¹²C labeling in CO (●) and in CH₄ (×) during the reaction of ¹³CO + H₂ at 493 K. The TPDE temperature was 493 K (■ stands for the sample obtained after extended evacuation).

Table III. ¹³CO + H₂ Reaction^a

TPDE, K	R_{CH_4} , mol s ⁻¹ (g of catalyst) ⁻¹	isotope composition of CH ₄
493	5.1×10^{-8} (1st)	¹² CH ₄ + ¹³ CH ₄
	8.1×10^{-8} (2nd)	¹³ C ₄
	9.0×10^{-8} (3rd)	¹³ CH ₄
553	9.9×10^{-8} (1st)	¹³ CH ₄
	1.1×10^{-7} (2nd)	¹³ CH ₄
	1.1×10^{-7} (3rd)	¹³ CH ₄

^a $T_{\text{reacn}} = 493$ K.

When decomposition of Ru₃(CO)₁₂/Al₂O₃ is performed up to 493 K, the reaction at 493 K with a H₂ + ¹³CO mixture takes place to form methane. The isotope fraction of methane and CO vs time is presented in Figure 7. As well as CO exchange, methane is formed initially in nonlabeled form and as the reaction proceeds more and more ¹³CO appears as methane. If more ¹²CO ligands are removed from the Ru subcarbonyl species before the reaction is started, e.g. by extended evacuation, more ¹³CO appears in the methane (see Figure 7b).

When the reaction is repeated on the same sample, no ¹²C-labeled methane appears in the gas phase, but this product is fully labeled. This implies that during the first reaction the Ru(CO)₂ species lost part of the CO ligands. Here it is important to note that under excess of hydrogen as is in the H₂ + ¹³CO mixture, at atmospheric pressure, CO ligands can be partly removed. Consequently, after the first reaction more metallic sites are generated and the methanation rate somewhat increases in the subsequent reaction as shown in Table III.

When decomposition occurs at 573 K with most of the CO ligands already removed during decomposition, after the first reaction only ¹³CH₄ is formed as indicated in the lower part of Table III. This obviously provides evidence of the participation of CO ligands in the methanation.

On the basis of isotope studies one might assume that CO hydrogenation takes place via dicarbonyl species. This is, however, contradicted by the inactivity of the Ru/Al₂O₃ sample, which is almost covered by Ru(CO)₂ species. The lack of catalytic activity suggests that the reaction is associated with metallic sites. Indeed, if the TPDE temperature is increased and standard conditions are used (flow mode, 5:1 H₂/CO mixture and 493 K temperature), the rate of methanation increases in parallel with the number of Ru metallic sites as determined by CO chemisorption as shown in Figure 8. This implies that the methanation is related to the free ruthenium sites.

The question now arising is why metallic ruthenium particles are more active in the presence of dicarbonyl species. The gradual appearance of the band at 1872 cm⁻¹ (Figure 6) assigned to bridged-type carbonyl species bound to two ruthenium atoms might be an answer to the question. Here, due to the weakened C-O bond, dissociation of CO to form reactive carbon may proceed more easily.

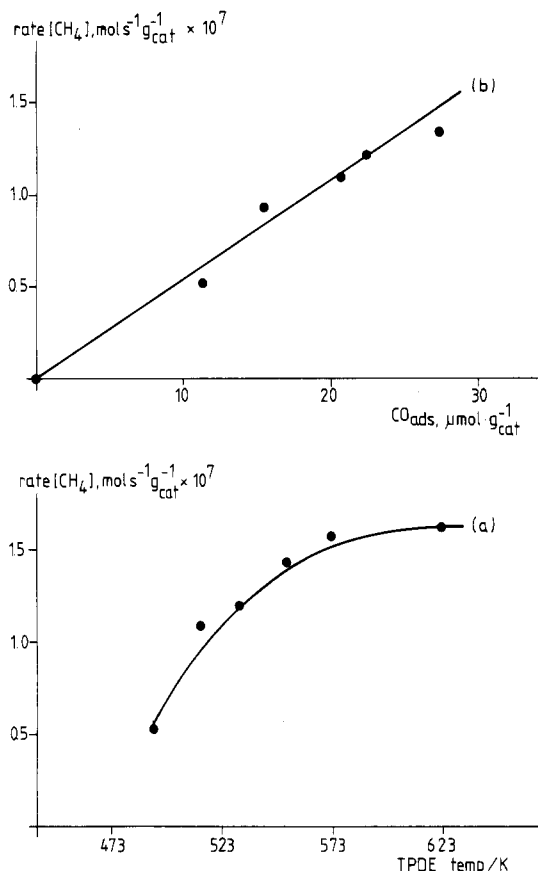


Figure 8. Methanation rate (a) vs the decomposition temperature in TPDE and (b) vs the amount of the CO chemisorbed at room temperature.

However, this is not supported by the ¹³CO experiments since bridged CO did not participate in molecular isotope exchange. A similar phenomenon was observed by Zanderighi et al.²⁵ using fully labeled CO in synthesizing Ru₃(¹³CO)₁₂. An extended study of the appearance of this band affected by various parameters showed that it is independent of the pretreatment of the alumina, the solvent used in impregnation, and the presence of air, water vapor, or oxygen at temperatures below 473 K. However, the band is always present if treatment is carried out at temperatures above 473 K and a trace quantity of oxygen is present in the helium. A set of experiments is shown in Figure 9. After decomposition of Ru₃(CO)₁₂ in unpurified He no dicarbonyl species are left (Figure 9a) but that associated with the band at 1872 cm⁻¹. When the same experiments are carried out in purified He, the opposite effect is observed (Figure 9b). When a switch is made to unpurified He, the original spectrum returns (Figure 9c). Admission of ¹³CO at 553 K (Figure 9d) results in the formations of ¹³CO dicarbonyl species, but no exchange occurs in the bridged species as indicated by the constancy of the band position at 1872 cm⁻¹. Obviously this band is not associated with any carbonyl species on the surface. The suggestion of transformation of Ru(CO)₂ into bridged CO with higher reactivity by use of free metallic sites can, therefore, be eliminated.

The second obvious suggestion would be a change in the mode of CO chemisorption during the reaction, e.g. from Ru(CO)₂ species into monoruthenium monocarbonyl species. In Figure 10 the CO stretching region under various conditions is shown. As demonstrated in Figure 10, during the reaction dicarbonyl species are maintained on the surface. The only obvious change is that Ru^{II}(CO)₂ is transformed into a more reduced form of dicarbonyl species, Ru⁰(CO)₂, indicated by a band pair at 2050 and 1975 cm⁻¹ (see Figure 10a-d). After evacuation and room-temperature

(25) Zanderighi, G. M.; Dossi, C.; Ugo, R.; Psaro, R.; Theolier, A.; Choplin, A.; D'Ornelas, L.; Basset, J. M. *J. Organomet. Chem.* **1985**, *296*, 127.

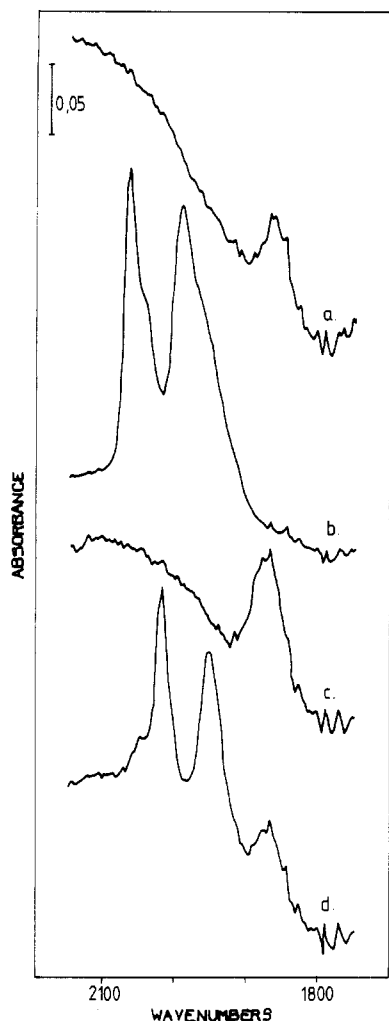


Figure 9. IR spectra of $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$: (a) after decomposition up to 573 K under He for 30 min; (b) after decomposition under purified He at 573 K for 30 min; (c) after treatment of the sample in (b) under He at 573 K for 30 min; (d) after recarbonylation of the sample in (c) with ^{13}CO at 553 K.

CO readmission a band structure similar to that observed without reaction (compare Figure 4 and Figure 10e–h) is visible. However, when $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ is reduced first in hydrogen at 635 K for 5 h after CO adsorption, a single CO band pattern is present (Figure 10i–k), similar to what was found by Kellner and Bell.¹⁷

4. Discussion

We did not aim to carry out a full structural analysis on the interaction between $\text{Ru}_3(\text{CO})_{12}$ and Al_2O_3 in the present investigations because it has been done for this system^{12,13,16,26,27} and also for mixed-metal clusters containing ruthenium.^{6,14,15,20} Here merely the conditions under which free ruthenium metal particles and ruthenium subcarbonyl species coexist were determined. Nevertheless, the structure of the subcarbonyl species and the valence state of ruthenium in the $\text{Ru}(\text{CO})_2$ entities as determined by IR spectroscopy are still relevant to the present study.

As far as the nature of the active sites of the cluster-derived $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst is concerned, three general conclusions can be drawn from the present investigations. First, metallic sites or free ruthenium atoms are prerequisite for the methanation reaction. Second, the bridged type of chemisorbed CO is not formed on the surface; therefore, it cannot be regarded as an intermediate during the $\text{CO} + \text{H}_2$ reaction. Finally, the difference in the ^{13}C content between CO and CH_4 species excludes the identity of the

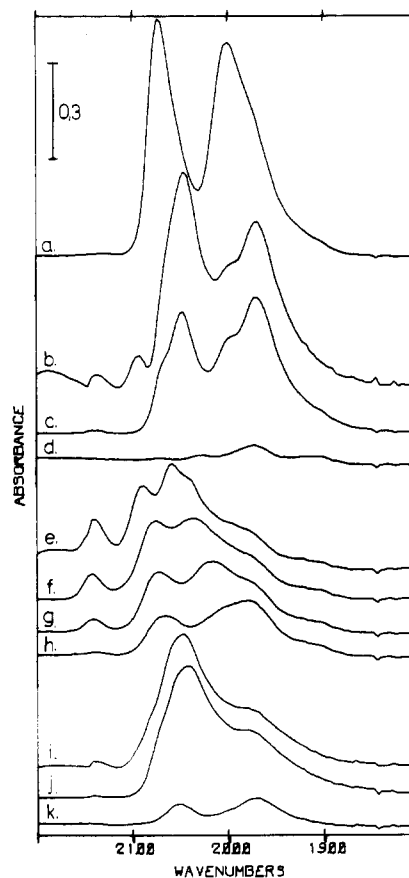


Figure 10. IR spectra of CO in $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$: (a) decomposition up to 523 K under vacuum for 30 min; (b) during $\text{CO} + \text{H}_2$ reaction of (a) at 493 K after 15 min; (c) (b) under vacuum at 493 K; (d) treatment of (c) between 623 and 723 K under vacuum for 20 min; (e) CO adsorption on (d) at 323 K; (f) evacuation of (e); (g) heating of (f) up to 473 K under vacuum; (h) heating of (f) up to 573 K under vacuum; (i) CO adsorption on (f) at 323 K after treatment at 623 K under H_2 for 5 h; (j) evacuation of (i); (k) heating of (j) up to 573 K.

surface species for the CO ligand exchange and the methanation reaction. This last statement, however, needs some further explanation. When the reaction of $\text{H}_2 + ^{13}\text{CO}$ is performed on a surface containing both $\text{Ru}(\text{CO})_2$ species and free ruthenium particles, three possibilities exist:

(i) Only Ru metal sites participate in the reaction. In this case the methane formed initially will be completely labeled.

(ii) Methanation proceeds via $\text{Ru}(\text{CO})_2$ species. Here, initially $^{12}\text{CH}_4$ and then $^{13}\text{CH}_4$ will be produced.

(iii) Fast exchange occurs between ^{13}CO gas and ^{12}CO ligands; the reactant and the resulting product will have a constant fraction of labeled molecules.

Although ruthenium sites are required for methanation, the experimental results still clearly indicate that CO ligands in $\text{Ru}(\text{CO})_2$ also participate in the methanation as will be discussed later. Concerning point ii, the isotope content of CO after a short initial period levels off while that of CH_4 during the reaction continuously decreases and is not identical with the ^{13}C content of CO; it is, therefore, very likely that for molecular exchange and for methanation different sites are needed. Further evidence for this statement is provided by the methanation rate being proportional to the metallic sites measured by the CO molecules chemisorbed on the samples (see Figure 8).

The following questions must also be addressed:

(i) Why is the metallic dispersion measured by CO chemisorption so low compared to that obtained by other measurements?

(ii) How can the difference revealed in the activity between the samples decomposed at low and high temperature be explained?

(iii) What is the explanation for the involvement of surface dicarbonyl species in the methanation reaction?

(26) Zecchina, A.; Guglielminotti, E.; Bossi, A.; Camia, M. *J. Catal.* **1982**, *74*, 225.

(27) Guglielminotti, E.; Zecchina, A.; Bossi, A.; Camia, M. *J. Catal.* **1982**, *74*, 252.

It is well-known²⁸⁻³¹ that ruthenium on alumina always forms an oxidic interface and its reduction is rather difficult. Even if the starting material is zerovalent ruthenium as in the case of Ru₃(CO)₁₂, after partial decomposition a part of the ruthenium becomes oxidized due to the reaction with surface OH⁻ and O²⁻ species. This is well demonstrated in the spectra of the chemisorbed CO molecule. As Figure 4 shows, a typical three-band spectrum is obtained similar to that observed on recarbonylation of the Cab-O-Sil-supported ruthenium clusters decomposed under hydrogen.⁶ This is due to the formation of Ru^{III}(CO)₂ and Ru^{II}(CO)₂ species,¹²⁻¹⁴ which is a result of the partial oxidation of the decomposed ruthenium framework under the effect of surface hydroxyl groups. On the other hand, if the decomposition of the Al₂O₃-supported Ru₃(CO)₁₂ cluster occurs under hydrogen at 770 K, larger metal particles are formed and the character of the CO chemisorbed is completely different from that presented in Figure 4. In this case the characteristic bands are as follows:²⁰ Ru^{III}(CO)₂, 2138 and 2070 cm⁻¹; Ru^{II}(CO)₂, 2072 and 2001 cm⁻¹; CO on Ru(0), 2050 cm⁻¹.

When the sample temperature is increased after CO chemisorption, decarbonylation of Ru^{III}(CO)₂, that is the most weakly bonded dicarbonyl species, occurs similarly to what was observed by Guglielminotti et al.¹² and the appropriate bands appear at 2075 and 2009 cm⁻¹ due to Ru^{II}(CO)₂. These are the same surface species as shown in Figure 2. Even high-temperature readmission of ¹³CO results in this two-band spectrum, indicating the rather high stability of the decarbonylated ruthenium species (see Figure 9d).

Since the surface contains oxidized ruthenium atoms to a large extent, determination of the metallic sites is difficult when no single CO peak at about 2050 cm⁻¹ is present.

However, under the reaction conditions nearly all surface ruthenium species with various oxidation states are converted into highly dispersed Ru(0) species indicated by the appearance of Ru⁰(CO)₂ with a band pair at 2050 and 1980 cm⁻¹ (see Figure 10b,c). After reaction and evacuation, the ruthenium species is partly oxidized again, so CO chemisorption results in the appearance of the bands characteristic of Ru^{III}(CO)₂ and Ru^{II}(CO)₂ (see Figure 10e,f). Consequently, determination of metallic dispersion in the presence of dicarbonyl species may not lead to an unambiguous result. Good estimation can only be obtained when CO chemisorption is characterized by a single CO band in the IR spectrum. It does not necessarily mean, however, that proportionality does not exist between the catalytic activity and the number of the CO molecules chemisorbed, but this cannot be utilized in the quantification of the turnover frequency (TOF).

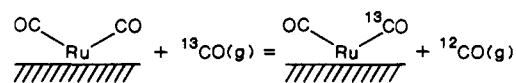
As an explanation for the activity difference between the samples prepared by heating to 573 and 773 K, the most obvious suggestion would be the difference in the modes of CO chemisorption during the reaction. Kellner and Bell¹⁷ already showed that two types of CO exist during the reaction: single-bonded and dicarbonyl species. However, this experiment cannot be related to the present work because, first, the IR spectra were taken under high pressure and, second, Kellner first completely decomposed Ru₃(CO)₁₂ and then the reaction was started. In those experiments linearly bound CO was considered to be the reaction intermediate.

In contrast to the experiments of Kellner and Bell,¹⁷ here practically no change was observed in the mode of CO chemisorption during the catalytic reaction except the change in ruthenium valence state. Although some decline in dispersion was experienced, the basic characteristics of the single ruthenium atoms were retained and the morphology of the metallic part was unchanged.

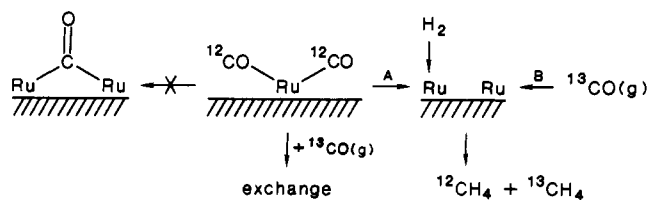
After long treatment at 623 K, which may mimic the decom-

Scheme I

1. $T \leq 473 \text{ K}$; $R_{\text{CH}_4}(473 \text{ K}) \ll 10^{-9} \text{ mol s}^{-1} (\text{g of catalyst})^{-1}$
(exchange only)



2. $473 \text{ K} < T < 573 \text{ K}$; $R_{\text{CH}_4} \approx 10^{-7} \text{ mol s}^{-1} (\text{g of catalyst})^{-1}$
(A faster than B)



position at 770 K, a change in the surface morphology can be observed characterized by CO chemisorption via the appearance of a dominating single CO band at 2050 cm⁻¹. It must be underlined that this morphology change could lead to an alteration in the catalytic activity.

The simplest interpretation of the activity differences between the Ru/Al₂O₃ samples prepared by decomposition of Ru₃(CO)₁₂ at 573 and 773 K is the various dispersions indicated by the mode of CO chemisorption. It is well known that the TOF for methanation over Ru/Al₂O₃ catalysts increases with decreasing dispersion.^{17,31,32} If we assume that the total number of ruthenium atoms are constant ($N_t = \text{constant}$), the total rate can be expressed as $R_{\text{CH}_4} = N_t C D (1 - D)$, where R_{CH_4} is the rate of methanation per gram of catalyst, C is a constant, and D is the dispersion defined by N_s/N_t . As the temperature used for the decomposition is increased, D will decrease and hence R should pass a maximum. This explains the activity decrease in the overall rate at lower dispersion.

Here the role of Ru(CO)₂ obviously is that metallic dispersion can be stabilized by this species whereas free ruthenium metal atoms formed at high temperature tend to be easily sintered. As is indicated by the easy change in the ruthenium valence state in the Ru(CO)₂ species, after partial removal of the CO ligands under the reaction conditions the metallic ruthenium remains in a well-dispersed state since the reaction temperature is not high (see Figure 9).

We still need to explain why ¹²CH₄ is produced initially from a H₂ + ¹³CO mixture during the catalytic methanation over a sample containing Ru(CO)₂ species. As was shown by the high rate of exchange, CO ligands in Ru(CO)₂ are already in a preactivated state. Thus, since there are free ruthenium sites on alumina, the CO molecules in CO ligands on the surface, being in a precursor state, might compete successfully for the neighboring Ru sites with the CO molecule arriving from the gas phase. This may be the most plausible explanation why ¹²CH₄ is the primary product followed by formation of ¹³CH₄. The lack of activity of a surface fully covered with Ru(CO)₂ species can be ascribed to the missing Ru sites, which are utilized for both CO and H₂ dissociation.

A tentative mechanism for the low- and medium-temperature reactivity of Ru(CO)₂ is presented in Scheme I.

When negligible numbers of ruthenium sites are present (after decomposition up to 473 K), the main reaction is the molecular CO exchange between the gaseous ¹³CO and the ligands in the Ru(CO)₂ species. This indicates that the CO molecules in the ligands are rather mobile. In the temperature range between 473 and 573 K, dicarbonyl species are present along with free ruthenium atoms in various oxidation states. This high ruthenium dispersion is stabilized by the presence of dicarbonyl species, and the valence of ruthenium can be easily converted into the zero state under the reaction conditions, i.e. in the presence of a CO

(28) Garbassi, F.; Bossi, A.; Orlandi, A.; Petrini, G.; Zanderighi, L. *Ned. Tijdschr. Vacuumtech.* **1978**, *16*, 35.

(29) Bossi, A.; Garbassi, F.; Orlandi, A.; Petrini, G.; Zanderighi, L. *Preparation of Catalysts*; Elsevier: Amsterdam, 1979; Vol. II, p 405.

(30) Kubicka, H. *React. Kinet. Catal. Lett.* **1976**, *5*, 223.

(31) Guzzi, L.; Schay, Z.; Matusek, K.; Bogay, I. *Appl. Catal.* **1986**, *22*, 289.

(32) Boudart, M.; McDonald, M. A. *J. Phys. Chem.* **1984**, *88*, 2185.

+ H₂ mixture. In the presence of metallic or zerovalent ruthenium atoms, CO ligands from the neighboring Ru(CO)₂ species can easily migrate to the free ruthenium sites, on which they dissociate and form methane.

The metallic ruthenium site is also a center for hydrogen dissociation and is a necessary requirement for the methanation reaction.

When decomposition takes place at high temperature (up to 773 K), all CO ligands which were required to stabilize single ruthenium atoms in dicarbonyl species are removed and the ruthenium particles tend to migrate on the surface to form large aggregates. On large particles the mode of CO chemisorption is changed; in particular, only a negligible amount of dicarbonyl species is produced.

In conclusion, it can be established that free ruthenium sites

are a necessary requirement for the CO hydrogenation reaction. Initially, the presence of dicarbonyl species in the temperature range in which the reaction takes place is important to stabilize the high dispersion of ruthenium. As soon as free ruthenium sites are also present, the CO molecules from the ruthenium dicarbonyl species indicated by the IR bands at 2072 and 2001 cm⁻¹ easily migrate to the free ruthenium sites due to their high mobility and react with hydrogen to produce methane. Since these molecules are already in an activated form, it explains their higher reactivity compared to those chemisorbed from the gas phase, i.e. ¹³CO. This ultimately leads to the initial ¹²CH₄ formation when H₂ + ¹³CO is used.

Registry No. Ru₃(CO)₁₂, 15243-33-1; Ru(CO)₂, 106960-32-1; Ru, 7440-18-8; CH₄, 74-82-8; H₃C(CH₂)₃CH₃, 109-66-0.

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Cyclotriphosphazenes with Geminal (Trimethylsilyl)methyl and Alkyl or Aryl Side Groups¹

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The synthesis of a series of organosilyl cyclophosphazenes of formula *gem*-N₃P₃Cl₄(CH₂SiMe₃)(R), where R = C₂H₅, *i*-C₃H₇, *n*-C₄H₉, *t*-C₄H₉, *neo*-C₅H₁₁, and C₆H₅, via organometallic reactions, is described. The chlorine atoms in the cyclic trimers were replaced by trifluoroethoxy groups by reactions that led to either retention of the (trimethylsilyl)methyl units or replacement of them by methyl groups, depending on the reaction conditions. The crystal and molecular structures of *gem*-N₃P₃Cl₄(CH₂SiMe₃)(*t*-C₄H₉) and the related derivative *gem*-N₃P₃Cl₄(CH₂SiMe₃)₂ were determined by single-crystal X-ray diffraction methods. Steric hindrance involving the organosilyl units results in a widening of the external angle at the supporting phosphorus atom and a narrowing of the corresponding ring angle at that site. Crystals of *gem*-N₃P₃Cl₄(CH₂SiMe₃)(*t*-C₄H₉) are orthorhombic with space group *Pbca*, with *a* = 14.884 (4) Å, *b* = 15.815 (4) Å, *c* = 16.615 (4) Å, *V* = 3910.9 Å³, and *Z* = 8. Crystals of *gem*-N₃P₃Cl₄(CH₂SiMe₃)₂ are monoclinic with space group *P2₁/n*, with *a* = 10.145 (4) Å, *b* = 11.060 (5) Å, *c* = 19.999 (6) Å, *β* = 103.56 (3)°, *V* = 2181.4 Å³, and *Z* = 4.

Introduction

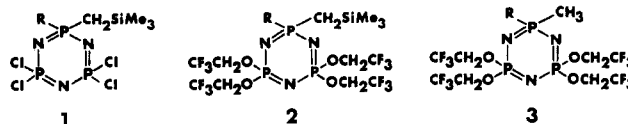
Cyclic and linear high-polymeric phosphazenes are now known that bear a wide variety of inorganic, organic, or organometallic side groups.^{2,3} A recent development has been the synthesis of phosphazenes with organosilicon side units.⁴⁻⁷ At the high-polymeric level⁶ these species are hybrid systems with characteristics that resemble those of both poly(organophosphazenes) and poly(organosiloxanes).

The main method for the preparation of phosphazene high polymers involves the ring-opening polymerization of small-molecule cyclic phosphazenes. Thus, the synthesis of phosphazene cyclic trimers or tetramers that bear organosilicon side groups is an essential first step in the assembly of hybrid organosilicon-organophosphazene macromolecules. A second reason for the study of small-molecule phosphazene ring systems is that they provide excellent reaction models for the more complex substitution reactions carried out on the corresponding high polymers. The small-molecule cyclic species also provide structural models for the high polymers since their molecular geometries can be deduced

more easily by X-ray diffraction techniques.

In earlier work⁵ at the cyclic trimer level, we developed a series of organometallic pathways that allowed access to small-molecule cyclotriphosphazenes with siloxane or (trimethylsilyl)methyl units linked to the phosphazene ring. In several cases, two identical organosilicon units were attached to one skeletal phosphorus atom. In other examples, a ring phosphorus atom bore one organosilicon unit and either a chlorine atom or a methyl group. The remaining four side groups were either chlorine atoms or trifluoroethoxy groups introduced by nucleophilic replacement of chlorine.

In the present work, we have extended the number of accessible structures to the 12 compounds depicted as species **1a-f** and **2a-f**. The compounds of formula **1** and **2**, where R = CH₃, were reported earlier.⁵ Species **3a-f** are compounds formed during the conversion of **1** to **2** by a pathway that will be discussed.



- (1) This is the fourth paper from our laboratory on organosilicon-organophosphazene chemistry. For the first three papers, see ref 4-6.
- (2) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic: New York, 1972.
- (3) Allcock, H. R. *Chem. Eng. News* **1985**, 63(11), 22.
- (4) Allcock, H. R.; Brennan, D. J.; Allen, R. W. *Macromolecules* **1985**, 18, 139.
- (5) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M.; Parvez, M. *Organometallics* **1986**, 5, 2434.
- (6) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M. *Macromolecules* **1988**, 21, 1.
- (7) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, 102, 2848.

- a R = C₂H₅
b *i*-C₃H₇
c *n*-C₄H₉
d *t*-C₄H₉
e *neo*-C₅H₁₁
f C₆H₅

In this study, we have attempted to answer the following questions: (a) What reaction pathways are available for the sequential replacement of two chlorine atoms in hexachloro-