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Structure of Propene in Heterogeneous Catalysis

I. Infrared Spectra of Propene Complexes of Some Atomic Metals[1]

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Propene–metal complexes are formed when excess propene is co-condensed with atomic nickel, palladium, iron, magnesium, or aluminum at liquid nitrogen temperature. Aluminum forms stable organoaluminum products that remain unchanged on warming to room temperature. Infrared spectra and hydrolysis experiments indicate the major product to be a C_3 alkane adduct of aluminum. Nickel, palladium, and iron give colorless, unstable π-propene complexes whose low-temperature infrared spectra resemble the spectrum of a propene analog of Zeise's salt $K(C_3H_6PtCl_3) \cdot H_2O$. Only an unstable, black, charge-transfer complex is obtained from magnesium, and its infrared spectrum is indistinguishable from that of solid propene. The charge-transfer complex and the π-propene complexes all decompose on warming into propene and metals.

INTRODUCTION

Direct spectroscopic observation of kinetically significant intermediates in heterogeneous catalytic reactions is severely hampered by low concentrations of such intermediates and by poor optical properties of catalysts and their support material. Thus, in the case of propene, which has served as a model in mechanistic studies (*1*) of olefin isomerization, hydrogen exchange, and hydrogenation reactions, identification of reaction intermediates by infrared spectroscopy has been successful only in the zinc oxide catalyst system (*2*). In the latter studies, Dent and Kokes (*2*) observed a new set of infrared bands when propene was adsorbed on zinc oxide, and, from isotopic data and an approximate normal coordinate analysis, deduced that these new bands originated from a π-allyl species coordinated to the zinc atom. From the analysis of products from isotopic propene reactions, they concluded, moreover, that this π-allyl species was the kinetic intermediate in isomerization, hydrogen exchange, and hydrogenation reactions of propene on the zinc oxide catalyst. A modification of this conclusion became necessary when Naito *et al.* (*3*) showed from microwave analysis of propene products that, while a π-allyl intermediate was consistent with product distributions in isomerization and hydrogen exchange reactions, the required intermediate or transition state in the hydrogenation reaction was a normal propene or a propyl species. Consequently, Chang *et al.* (*4*) proposed for the latter intermediate a weakly bonded surface propene which showed only a single new infrared band at 1620 cm^{-1}. Additional complexities of this catalyst system were pointed out more recently by Nguyen and Sheppard (*5*) who provided spectroscopic evidence that the major surface species was not a neutral π-allyl but a symmetric allyl anion. These authors also suggested the possible presence of species of different structure since more absorption bands were present in the poorly transmitting infrared region below 1000 cm^{-1}. Hence, even in this well-studied system of propene on zinc

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oxide, many surface species evidently are present and their assignments as intermediates in various catalytic reactions are still not very clear. The present series of investigations, therefore, was undertaken to obtain more complete spectroscopic data on propene adsorbed on metal catalyst surfaces and to correlate these surface species with specific catalytic reactions.

The experimental procedure adopted here attempts to overcome limitations encountered by earlier investigators and is based on the pioneering studies of Skell and co-workers (*6*) on metal atom chemistry. These investigators have shown that stable and unstable olefin–metal atom complexes are formed when atomic metals are codeposited with excess olefin at liquid nitrogen temperature and that many of these complexes give products similar to those from catalytic reactions on bulk metals. For example, Skell *et al.* (*7*) have generated at liquid nitrogen temperature an unstable nickel propene complex that did not survive warm-up to room temperature but was hydrogenated by water and gave decomposition products arising from inter- and intramolecular hydrogen exchange reactions. In the present series of studies these low-temperature matrices of olefin-containing atomic metals and the fates of such matrices on warming were examined by infrared spectroscopy. In this paper, the spectra of propene complexed with atomic nickel, palladium, iron, magnesium, and aluminum are presented and interpreted.

EXPERIMENTAL

Propene from the Matheson Company was degassed and distilled under reduced pressure in a vacuum line. Palladium (99.5%) and magnesium (99.9%) metals came from Research Organic and Inorganic Chemical Corporation, and metallic nickel (99.9%) was from Alfa Inorganic Company. The source of electrolytic iron powder was Fisher Scientific Company, and that of the aluminum foil (ACS reagent) was Baker and Adamson Company. All metals were used directly. Propene-d_6 and propene-3,3,3-d_3 were from Merck Sharpe & Dohme of Canada, Ltd., and their infrared spectra indicated satisfactory isotopic purity for direct use.

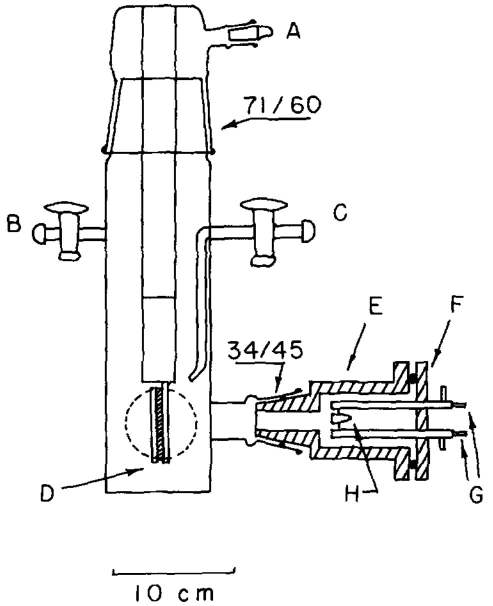


FIG. 1. Low-temperature infrared cell. See text for description of parts.

The low-temperature infrared cell, illustrated in Fig. 1, was a modified Wagner–Hornig-type (*8*) Pyrex glass cell. The glass portion was fabricated around a 71/60 standard taper joint, and it consisted of a thermocouple wire port A, a cell pump-out port B, a matrix gas inlet C, and a 34/45 standard taper inlet to which the metal vaporization unit was attached through an o-ring. The vaporization unit was made of brass in two sections E and F. The plate section F supported water-cooled copper electrodes G and an alumina-coated tungsten wire crucible H. Electrode tubes were sealed to the end plate with epoxy cement which provided satisfactory electrical insulation and vacuum seal. Machine screws held the crucible to the electrodes. Several windings of copper tubings were soldered on the outer faces of E and F to allow water cooling during the metal vaporization process. The end plate F with an o-ring was secured to the body unit E with machine bolts.

A cylindrical copper cup soft-soldered to and extending from a Pyrex glass-to-copper seal or Pyrex glass-to-Kovar metal seal served as the cold finger. A copper window bracket silver-soldered directly to the cold finger held a CsBr or CsI window as shown in Fig. 1. A copper–constantan thermocouple junction attached to the lower corner of the window frame gave the window temperature (9).

Sample depositions were carried out in the following manner. After the metal crucible system was degassed and the cell pressure was below 10^{-4} Torr, the cold finger was filled with liquid nitrogen which gave a typical temperature of −190°C at the sample window. The propene matrix gas was introduced from a storage bulb on the vacuum line through a needle valve, and then through inlet C (Fig. 1) onto the cooled window. The rate of deposition was controlled to give initially a transparent film. As soon as the matrix introduction was started, the power to the metal vaporization unit was increased to 200–400 W for nickel, palladium, and iron, and about 100 W for aluminum and magnesium. Sample deposition times ranged from about 30 min to nearly 3 hr. Although metal atom concentrations could not be measured, product yields in the present and many other studies with this cell suggested a matrix-to-metal atom mole ratio of about 10/1 in the most concentrated samples and about 100/1 in typical samples. These concentrations were higher than those in the usual matrix isolation technique but they gave thinner matrix samples whose infrared spectra were obscured only in the regions of intense matrix bands. Upon completion of deposition, the entire cell was removed from the vacuum line, the cold finger was rotated, and the infrared spectrum was scanned on Perkin–Elmer grating instruments model 521 or 225. After initial scans samples were warmed to various temperatures by removing the refrigerant and then recooled again to record their spectra. Some samples after warming to room temperature were recondensed on the cooled window or were analyzed by gas chromatography or mass spectroscopy.

RESULTS

Propene matrices prepared under identical experimental conditions but without metal atoms were colorless and transparent to the visible light. Its typical infrared spectrum recorded at liquid nitrogen temperature is illustrated in Fig. 2. On warming, propene first liquefied and then began to distill off the window at about −160°C, thereby making it possible to remove the matrix at low temperatures. With nickel, palladium, or aluminum atoms in the matrices, samples first appeared colorless but as their metal content increased they developed an amber color. Samples with iron were brown from the start and then became black as their thicknesses increased. Magnesium samples were initially gray but they too became black at higher metal concentrations. In all cases regardless of their colors, these matrices with metal atoms initially showed excellent transmission throughout the infrared region.

The initial infrared spectra of propene matrices containing atomic nickel, palladium, iron, or aluminum showed new absorption bands. As these matrices were warmed to temperatures where the propene matrix bands began to decay, relative intensities of new bands first increased slightly, indicating formation of more products, and then remained constant while propene bands continued to decay. Thus, the new products were relatively stable at temperatures where propene itself distilled off the sample window. Further increase in sample temperature caused the new bands to decay except in the aluminum system where the new bands remained unchanged to room temperature. The decay of the new infrared bands in nickel, palladium, and iron systems became appreciable at about −140,

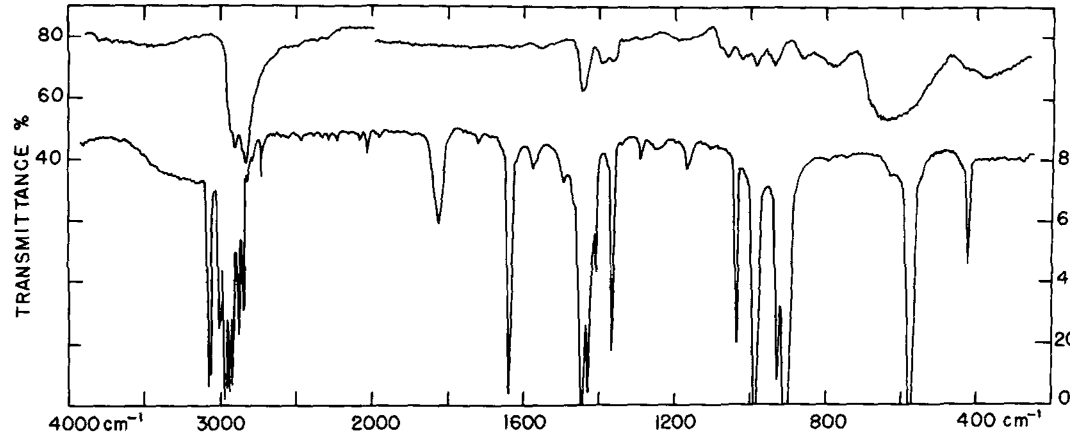


FIG. 2. Infrared spectrum of propene. Lower spectrum: free propene at −190°C. Upper spectrum: aluminum complex at 35°C.

−120, and −80°C, respectively, and concomitantly the infrared transmission of the window decreased due to precipitation of the metal. Comparison of changes in relative intensities of new bands during this decay indicated the formation of a single product in each metal system. At room temperature the spectra of window residues showed no absorption bands arising from organic groups and the spectra of recovered matrix samples were identical to that of propene alone. Therefore, unstable propene–metal complexes were formed in nickel, palladium, and iron systems but the aluminum system gave stable reaction products.

The infrared spectrum of products obtained from reactions of propene with atomic aluminum is shown in Fig. 2 and peak frequencies are summarized in Table 1. When this sample was exposed to water vapor, not only did all of its infrared bands disappear but both condensable and noncondensable gaseous products were obtained. A gas chromatographic analysis of one sample of condensable products showed its composition to be propane (68%), propene (19%), 2,3-dimethylbutane (10%), 2-methylpentane (3%), and hexane (0.2%). These products and their relative yields are similar to those obtained earlier by Skell and Wolf (*10*) from an alkyl aluminum compound prepared under equivalent experimental conditions. The noncondensable gas may be hydrogen which Skell and Wolf also reported.

Spectra of propene complexes with atomic nickel, palladium, and iron are displayed in Fig. 3. Most free propene in these samples had been removed by warming one or more times to −143°C (Ni, Pd) or to −107°C (Fe) and then recooling for infrared scans. The sharp peak near 1640 $\mathrm{cm^{-1}}$ in each spectrum of Fig. 3 is due to residual uncomplexed propene still trapped in the solid. These small amounts of free propene could be reduced further by warming but usually at the expense of some loss of the unstable complexes. Absorption frequencies of these propene–metal complexes are listed in Table 1. Additional infrared data on nickel complexes of propene-d_6 and propene-3,3,3-d_3 were obtained and fundamental vibrational frequencies of these free and complexed propenes at liquid nitrogen temperature are summarized in Table 2.

According to Skell and co-workers (*7*) the unstable propene–nickel complex hydrolyzes to give propane and propene in a 1 : 4 ratio and a C_3-hydrocarbon-to-nickel ratio of 2 : 1. The unstable nickel complex prepared in the present study also hydro-

TABLE 1

Infrared Spectra of Some Propene–Metal Complexes (in cm^{-1})

C_3H_6/Al 35°C	C_3H_6/Ni −190°C	C_3H_6/Pd −190°C	C_3H_6/Fe −190°C	$K(C_3H_6PtCl_3) \cdot H_2O$[a] 25°C	$(C_3H_6PtCl_2)_2$[a] 25°C
	3073 w	3073 w	3073 w	3068 m	3071 w
	3044 m	3054 m	~3034 m	3034 w	3039 w
	2996 m	3006 m	~2996 vw	3010 m	3012 w
~2940 vs	2956 s	2961 s	2956 s	2965 m	2988 w
2915 vs	2931 s	2938 s	2928 s		2954 w
	2901 m	2904 m		2911 vw	2901 vw
~2870 vs	2876 m	2876 m	2874 s		
2840 vs	2846 m	2846 m	2846 s		
	1516 s	1528 s	~1483 m	1504 s	1504 s
1445 s	1448 vs	1448 s	1448 s	1449 s	1447 s
	1432 s	1432 s	~1428 m	1429 s	1431 s
	1410 w	~1412 vw	~1414 w		
1390 m	1388 m	1394 m	~1378 m	1392 m	1395 s
1366 m	1361 m	1365 m	1366 s	1365 s	1361 s
~1270 w	1242 vs	1247 s	~1214 s	1252 w	1243 vw
	~1217 w		~1187 m		
~1170 w	1154 w	1164 w	1149 s	1175 m	1171 vw
1060 m	1032 vs	1035 vs	1029 vs	1049 s	1045 s
~1020 w				1010 s	1010 s
990 w	992 s	993 m	993 m	990 s	995 s
	~978 w	~973 w			
935 m	930 s	928 s	934 m	932 s	929 s
	908 vs	910 s	904 vs		
	883 vs	896 s	~878 m	899 s	898 s
~860 w					877 w
			~838 w		820 w
	~818 w	~823 w	~808 w	809 s	807 w
				800 w	
~760 m	~749 w	~726 w	~709 vw		
~640 vs		~649 vw	~659 vw		
	581 s	582 m	579 m		
	468 m	462 w	~460 w		
~390 w	426 w	429 w			
	359 vs	305 s	352 m		
			306 w		
		279 w	280 vw		
	~250 m	247 w	250 vw		
			220 vw		

[a] From Ref. (*16*). Data extend only to 700 cm^{-1}. Water bands at 3460 vs, 3217 w, and 1621 s are not listed for the potassium salt.

lyzed and gave propane, but the small sample sizes precluded determination of propene-to-metal atom ratios. For example, the yield of propane from the hydrolysis of the nickel sample whose spectrum is shown in Fig. 3 was only about 5% of the total propene used in the original matrix. This yield gives a matrix-to-metal mole ratio of about 10/1 in the original sample.

Infrared spectra of propene matrices con-

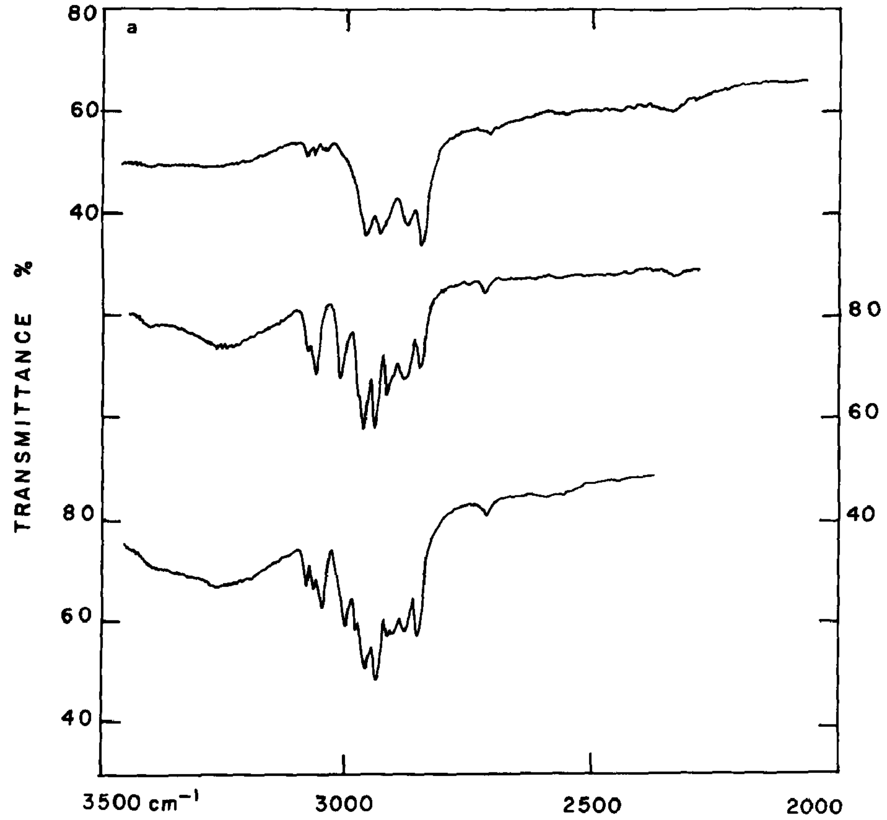


FIG. 3a. Infrared spectra of propene–metal complexes at −190°C. Lower spectrum: nickel complex. Middle spectrum: palladium complex. Upper spectrum: iron complex.

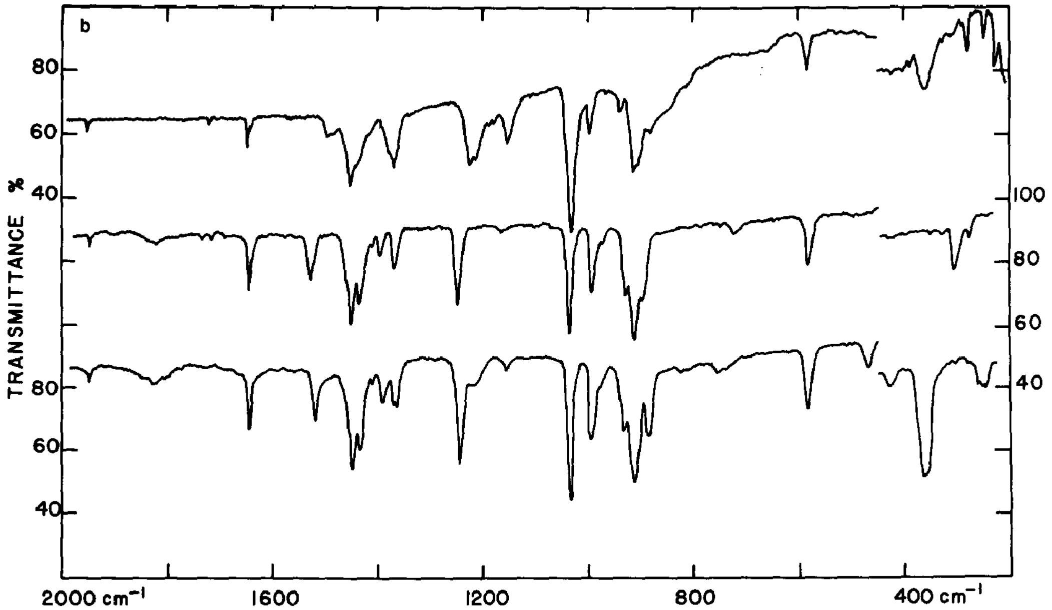


FIG. 3b. Infrared spectra of propene–metal complexes at −190°C. Lower spectrum: nickel complex. Middle spectrum: palladium complex. Upper spectrum: iron complex.

TABLE 2

Fundamental Frequencies of Free and Complexed Propenes (−190°C, cm^{-1} Units)

Modes[a]	$CH_{3CH}{=}CH_2$	$CD_3CD{=}CD_2$	$CD_3CH{=}CH_2$	$CH_3CH{=}CH_2$/Ni	$CD_3CD{=}CD_2$/Ni	$CD_3CH{=}CH_2$/Ni
Stretch(CH_2)	3073	2315	3095	3044	2300	3095
Stretch(CH)	3010	2245	3010	2996	2220	3010
Stretch(CH_2)	2990	2200	2984	2956	2195	2984
Stretch(CH_3)	2935	2230	2226	2931	2220	2226
Stretch(CH_3)	2880	2120	2070	2876	2110	2070
Stretch(CC)	1640	1582	1642	1242	1423	1242
Bend(CH_3)	1456	1040	1038	1448	1040	1038
Bend(CH_2)	1430	1013	1418	1516	995	1510
Bend(CH_3)	1367	1040	1060	1388	1040	1060
Bend(CH)	1290	960	1296	1361	911	1346
Stretch(CC)	1164	1142	1157	1154	1137	1115
Rock(CH_3)	936	710	777	933	709	777
Rock(CH_2)	930	777	860	930	777	860
Bend(CCC)	424	350	390	468	350	390
Stretch(CH_3)	2960	2200	2195	2901	2195	2195
Bend(CH_3)	1440	1040	1050	1432	1040	1050
Wag(CH_3)	1040	870	872	1032	846	826
Wag(CH)	995	732	1000	992	730	996
Wag(CH_2)	906	710	913	883	710	913
Twist(CH_2)	577	437	530	581	440	530
Twist(CH_3)	—	—	—	—	—	—
Stretch(M–C)	—	—	—	426	420	—
Stretch(M–C)	—	—	—	359	337	350

[a] Assignments and normal mode descriptions for free propenes are based on Refs. (*17*, *18*).

taining magnesium atoms were indistinguishable from that of propene itself even when magnesium concentrations were high enough to make such samples resemble carbon black. Warming of these samples caused propene absorption bands to disappear but without formation of any new peaks. At the same time the transmission of the window decreased as the metal precipitated. Only dark metallic residues remained on the sample window at room temperature, and it hydrolyzed to give magnesium hydroxide and a noncondensable gas presumably hydrogen.

DISCUSSION

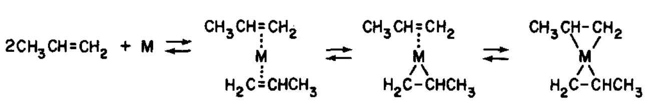
Skell and Wolf (*10*) have already discussed in detail possible structures of organoaluminum products from the co-condensation of propene with atomic aluminum. The principal product was a C_3 alkane adduct resulting from addition of one aluminum atom to the propene double bond. The conspicuous absence of olefinic CH stretch bands above 3000 cm^{-1} and of the C=C stretch band at 1640 cm^{-1}, as well as the presence of a characteristic Al—C stretch band (*11*) at 640 cm^{-1} in the spectrum of Fig. 2, is completely consistent with this adduct. The C_6 hydrocarbons from the hydrolysis are attributed to coupling reactions of partially hydrolyzed 1-propyl and 2-propyl ligands. Propene and hydrogen are presumably thermal decomposition products formed during the exothermic hydrolysis reactions since Skell and Wolf (*10*) found in D_2O hydrolysis isotopic compositions of propane of 86% d_2 and of propene of 56% d_0 and 41% d_1.

Infrared spectra of unstable propene complexes of nickel, palladium, and iron, shown in Fig. 3, are very different from the spectra of π-allyl complexes $(C_3H_5)_2Ni$ (*12*), $(C_3H_5)_2Pd$ (*12*), $(C_3H_5PdCl)_2$ (*13*), $(C_3H_5PdBr)_2$ (*13*), and $C_3H_5Mn(CO)_4$ (*14*), or of the allyl anion complexes (*15*) C_3H_5Li,

C_3H_5Na, and $(C_3H_5)_2Mg$. However, they show a remarkable resemblance to the spectra of stable propene analogs of Zeise's salt and its dimer, $K(C_3H_6PtCl_3) \cdot H_2O$ and $(C_3H_6PtCl_2)_2$. The infrared spectra of these salts have been reported by Chatt and Duncanson (*16*) and their frequencies are listed in Table 1. Comparison of data in this table leaves no doubt that the ligands in the unstable complexes of Fig. 3 are π-propenes.

Assignments of fundamental vibrational modes of solid uncomplexed isotopic propenes and their π-propene–nickel complexes are summarized in Table 2. Although considerable uncertainties still exist in assignments of isotopic propenes, choices listed in this table are based on more recent studies of these molecules by Abe (*17*) and by Silvi *et al.* (*18*). The perturbed C=C stretch and metal–carbon stretch modes in the π-complexes were located according to Hiraishi's spectroscopic study (*19*) of isotopic Zeise's salts $K(C_2H_4PtCl_3) \cdot H_2O$, $K(C_2D_4PtCl_3) \cdot H_2O$, and the dimeric species $(C_2H_4PtCl_2)_2$.

Propene matrices containing magnesium atoms did not show any new infrared bands but their dark colors suggest the formation of unstable charge-transfer-type magnesium–propene complexes. Colors in matrices with other metal atoms must originate also from such unstable charge-transfer species. Thus, according to the experimental observations from the present work and the stoichiometric coefficient of 2 established by Skell and co-workers (*7*) for the propene/nickel ratio in the nickel complex, the following sequence of reversible reactions must be taking place in propene matrices containing metal atoms M.



Only the first step forming the charge-transfer species was effective with magnesium, but with other metals the presence of color and new infrared bands suggest that reactions at least to the second product had occurred during the deposition of the samples. A slight increase in intensities of π-propene infrared bands and a concomitant bleaching of color require the last reaction step. The reversibility of each step in the sequence accounts for the decompositions of complexes into propene and metals. During the decompositions of the nickel and magnesium complexes, double-bond isomerization in the propene ligand was observed. A spectroscopic study of this isomerization reaction will be described in the next report.

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REFERENCES

1. Kondo, T., Saito, S., and Tamaru, K., *J. Amer. Chem. Soc.* **96,** 6857 (1974).
2. Dent, A. L., and Kokes, R. J., *J. Amer. Chem. Soc.* **92,** 6709 and 6718 (1970).
3. Naito, S., Kondo, T., Ichikawa, M., and Tamaru, K., *J. Phys. Chem.* **76,** 2184 (1972).
4. Chang, C. C., Conner, W. C., and Kokes, R. J., *J. Phys. Chem.* **77,** 1957 (1973).
5. Nguyen, T. T., and Sheppard, N., *J. Chem. Soc. Chem. Commun.*, 868 (1978).
6. Skell, P. S., *Proc. Int. Union Pure Appl. Chem. XXIIIrd* **4,** 215 (1971).
7. Skell, P. S., Havel, J. J., Williams-Smith, D. L., and McGlinchey, M. J., *J. Chem. Soc. Chem. Commun.*, 1098 (1972).
8. Wagner, E. L., and Hornig, D. F., *J. Chem. Phys.* **18,** 296 (1950).
9. Hull, L. A., Hisatsune, I. C., and Heicklen, J., *J. Amer. Chem. Soc.* **94,** 4856 (1972).
10. Skell, P. S., and Wolf, L. R., *J. Amer. Chem. Soc.* **94,** 7919 (1972).
11. Pitzer, K. S., and Sheline, R. K., *J. Chem. Phys.* **16,** 552 (1948).

12. Andrews, D. C., and Davidson, G., *J. Organomet. Chem.* **55,** 383 (1973).

13. Sourisseau, C., and Pasquier, D., *Canad. J. Spectrosc.* **18,** 91 (1973).

14. Davidson, G., and Andrews, D. C., *J. Chem. Soc. Dalton Trans.*, 126 (1972).

15. Sourisseau, C., and Pasquier, D., *Spectrochim. Acta Part A* **31,** 287 (1975).

16. Chatt, J., and Duncanson, L. A., *J. Chem. Soc.*, 2939 (1953).

17. Abe, K., Ph.D. thesis in chemistry, Faculty of Science, The University of Tokyo, 1970.

18. Silvi, B., Labarbe, P., and Perchard, J. P., *Spectrochim. Acta Part A* **29,** 263 (1973).

19. Hiraishi, J., *Spectrochim. Acta Part A* **25,** 749 (1969).