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Synthesis, Characterization, and Cleavage Reactions of Substituted Cyclopropenium Salts of $Pt_2Cl_6^{2-}$ and $Pd_2Cl_6^{2-}$

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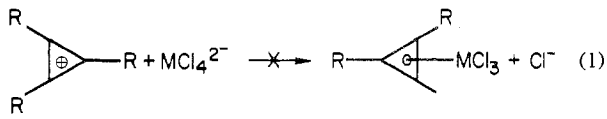
Salts of the type $(R_3C_3^+)_2(M_2Cl_6^{2-})$, where R = $(CH_3)_2N$ or n-C_3H_7 and M = Pt or Pd, have been prepared and characterized spectroscopically. ^{1}H nmr spectra suggest cation–anion association in solution as the cyclopropenium chemical shifts of the $M_2Cl_6^{2-}$ salts are consistently 0.1–0.5 ppm downfield of the salts containing other anions. The equilibrium constant for the symmetric cleavage reaction $M_2Cl_6^{2-} + 2L \rightleftharpoons 2LMCl_3^-$ is about five orders of magnitude larger for Pt than Pd when L is acetonitrile or cyclooctene. Reaction of $Pd_2Cl_6^{2-}$ with cyclooctene is subject to a striking counterion effect. When $[(CH_3)_2N]_3C_3^+$ is the counterion, a smooth one-step transformation to $(C_8H_{14})PdCl_3^-$ is observed. When the cation is $(n\text{-}C_3H_7)_3C_3^+$, a spectrophotometric titration shows the buildup of an intermediate product. The visible spectrum of this intermediate is consistent with a monochloro-bridged structure, $(C_8H_{14})Cl_2Pd\text{–}Cl\text{–}PdCl_3^{2-}$. It is speculated that the intermediate is stabilized by some type of specific association with $(n\text{-}C_3H_7)_3C_3^+$. The final product is again $(C_8H_{14})PdCl_3^-$.

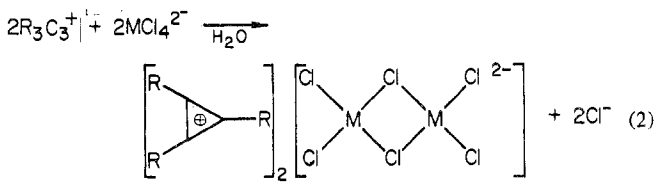
Introduction

While attempting to prepare neutral π-cyclopropenium complexes[1] by direct substitution of $R_3C_3^+$ for Cl^- in MCl_4^{2-} (eq 1), we isolated, instead, cyclopropenium salts (I–IV) of



(1)

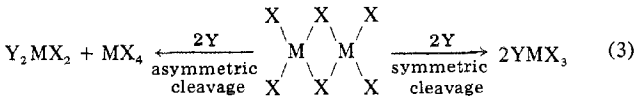
the binuclear anions $Pt_2Cl_6^{2-}$ and $Pd_2Cl_6^{2-}$ (eq 2).



(2)

I, M = Pt, R = $(CH_3)_2N$
II, M = Pt, R = n-C_3H_7
III, M = Pd, R = $(CH_3)_2N$
IV, M = Pd, R = n-C_3H_7

It has been established that the anion $Pt_2Br_6^{2-}$ has a planar, dihalo-bridged structure.[2,3] Cleavage reactions of $Pt_2Br_6^{2-}$ occur symmetrically with monodentate amines and olefins and asymmetrically with the bidentate olefin 1,5-cyclooctadiene (eq 3).[4,5] A mechanistic scheme has been proposed[4,5]



(3)

for these cleavage reactions which features an associative rate-determining step to give a monohalo-bridged intermediate. Such an intermediate, however, has not been observed previously.

We have characterized complexes I–IV and studied their cleavage reactions with acetonitrile and cyclooctene. In the symmetric cleavage reaction of cyclooctene with IV, an intermediate is observed, which apparently is stabilized by the $(n\text{-}C_3H_7)_3C_3^+$ counterion. Evidence that this intermediate possesses a monohalo-bridged structure is presented in this paper as part of the spectroscopic and reactivity studies of I–IV.

Experimental Section[6]

Tripropylcyclopropenium Tetrafluoroborate, $[(n\text{-}C_3H_7)_3][BF_4]$. This white salt was prepared by the method that Breslow, Hover, and Chang[7] used to prepare the corresponding perchlorate, substituting triphenylmethyl tetrafluoroborate for triphenylmethyl perchlorate. The crude product was obtained in 60% yield and crystallized from ethyl acetate–diethyl ether; mp 148°. *Anal.* Calcd for $C_{12}H_{21}BF_4$: C, 57.17; H, 8.40. Found: C, 57.27; H, 8.55.

Tris(dimethylamino)cyclopropenium Tetrafluoroborate, $\{[(CH_3)_2N]_3C_3\}\{BF_4\}\cdot{}^1/_2H_2O$. This was prepared using the procedure described by Yoshida and Tawara[8] for the preparation of the anhydrous perchlorate. To a solution of 10 g (0.071 mol) of C_3Cl_4 in 100 ml of CH_2Cl_2 cooled to 0° was added dropwise with stirring *ca.* 40 ml (0.6 mol) of dimethylamine. As the very vigorous initial reaction subsided, the remaining dimethylamine was added as rapidly as possible. The flask was then tightly stoppered. The mixture was stirred 3 hr at 0° and 15 hr at room temperature and then was refluxed 5 hr. The mixture was cooled to 0°, shaken well with 200 ml of 50% aqueous HBF_4, separated, dried over $MgSO_4$, and concentrated to dryness on a rotary evaporator. The waxy, pink residue was crystallized from 22 ml of $CHCl_3$ to give 5.1 g (35%) of white product after drying. No attempt was made to maximize this yield. The ir spectrum showed very strong H_2O absorption even after drying the sample 3 days at 5-μ pressure. The nmr spectrum showed no $CHCl_3$ of crystallization present. The analysis corresponds to $\{[(CH_3)_2N]_3C_3\}\{BF_4\}\cdot{}^1/_2H_2O$, mp 116–120°. *Anal.* Calcd for

(1) π-Cyclopropenium complexes reported through 1972 can be found in the following references: (a) E. W. Gowling and S. F. A. Kettle, *Inorg. Chem.*, **3**, 604 (1964); (b) R. M. Tuggle and D. L. Weaver, *ibid.*, **10**, 1504, 2599 (1971); (c) D. L. Weaver and R. M. Tuggle, *J. Amer. Chem. Soc.*, **91**, 6506 (1969); (d) M. D. Rausch, R. M. Tuggle, and D. L. Weaver, *ibid.*, **92**, 4981 (1970); (e) W. K. Olander and T. L. Brown, *ibid.*, **94**, 2139 (1972); (f) R. G. Hayter, *J. Organometal. Chem.*, **13**, P1 (1968); (g) P. S. Welcker and L. J. Todd, *Inorg. Chem.*, **9**, 286 (1970); (h) I. I. Moiseev, M. N. Vargaftik, and Ya. A. Syrkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 775 (1964).

(2) C. M. Harris, S. E. Livingstone, and N. C. Stephenson, *J. Chem. Soc.*, 3697 (1958).

(3) N. C. Stephenson, *Acta Crystallogr.*, **17**, 587 (1964).

(4) M. M. Muir and E. M. Cancio, *Inorg. Chim. Acta*, **4**, 565 (1970).

(5) R. G. Pearson and M. M. Muir, *J. Amer. Chem. Soc.*, **88**, 2163 (1966).

(6) Melting points were determined using open capillary tubes and are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Analytical samples were crystallized 3 times. Nuclear magnetic resonance spectra were recorded on a Varian A-60A spectrometer operating at *ca.* 40° and ultraviolet–visible absorption spectra were determined with a Cary 17 spectrometer operating at *ca.* 21°. Infrared spectra (4000–300 cm^{-1}) were recorded on a Perkin-Elmer 225 spectrometer using a Beckman Variable Temperature Unit, VLT-2, modified to hold KBr pellets for liquid nitrogen temperature spectra. Far infrared spectra (400–33 cm^{-1}) were recorded with a Perkin-Elmer 180 spectrometer. Raman spectra were obtained with a Cary 81 spectrometer equipped with a 6328-Å He–Ne laser with 60–100 mW output. Conductivities were determined with a Radiometer type CDM2e conductivity meter and a cell of cell constant 0.57 cm.

(7) R. Breslow, H. Hover, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).

(8) Z. Yoshida and Y. Tawara, *J. Amer. Chem. Soc.*, **93**, 2573 (1971).

Table I. Nmr Measurements

Compd	Solvent	Chem shift, ppm (downfield of internal TMS)		
		α-CH_2	β-CH_2	CH_3
$[(n\text{-}C_3H_7)_3C_3][BF_4]$[a]	$(CD_3)_2CO$	3.32	*l*	1.08
	CH_2Cl_2	3.15	1.92	1.08
	CH_3CN	3.16	1.90	1.06
	$CHCl_3$	3.16	1.92	1.07
$[(n\text{-}C_3H_7)_3C_3][Br]$[a]	$CHCl_3$[b]	3.26	1.90	1.03
$[(n\text{-}C_3H_7)_3C_3]_2[Pt_2Cl_6]$[a]	$(CD_3)_2CO$	3.67	2.18	1.16
	CH_2Cl_2[c]	3.67	2.15	1.16
$[(n\text{-}C_3H_7)_3C_3]_2[Pd_2Cl_6]$[a]	$(CH_3)_2CO$	3.65	*l*	1.17
	CH_2Cl_2	3.58	2.15	1.19
$[(n\text{-}C_3H_7)_3C_3][(CH_3CN)PtCl_3]$[a]	CH_3CN[d]	3.28	1.97	1.07
$\{[(CH_3)_2N]_3C_3\}\{BF_4\}$[e]	$(CD_3)_2CO$			3.20
	CH_2Cl_2			3.14
	$(CD_3)_2SO$			3.07[f]
	$CHCl_3$[g]			~3.1
$\{[(CH_3)_2N]_3C_3\}\{Cl\}$[e]	CH_2Cl_2			3.19[h]
$\{[(CH_3)_2N]_3C_3\}\{B(C_6H_4)_4\}$[e]	CH_2Cl_2[i]			2.92
	$(CH_3)_2CO$			3.03
$\{[(CH_3)_2N]_3C_3\}_2\{PtCl_4\}$[e]	CH_2Cl_2			3.25
$\{[(CH_3)_2N]_3C_3\}_2\{Pt_2Cl_6\}$[e]	CH_2Cl_2[c]			3.39
$\{[(CH_3)_2N]_3C_3\}_2\{Pd_2Cl_6\}$[e]	CH_2Cl_2			3.41
$\{[(CH_3)_2N]_3C_3\}\{(CH_3CN)PtCl_3\}$[e]	CH_3CN[j]			3.08
	CH_2Cl_2[k]			3.22

[a] All $[(n\text{-}C_3H_7)_3C_3]$ salts showed a triplet-sextet-triplet pattern for the α-CH_2, β-CH_2, and CH_3 peaks, respectively. All coupling constants are *ca.* 7.5 Hz. [b] Chemical shifts for this salt were based on an assigned value of 7.27 ppm for the shift of solvent. [c] Examination of the nmr spectrum at 31, 13, −36, and −62° showed no changes except for decrease of the signal due to sample crystallization. [d] Chemical shift of coordinated CH_3CN is 2.39 ppm. $J_{^{195}Pt-^1H} = 15$ Hz. [e] All $\{[(CH_3)_2N]_3C_3\}$ salts show single CH_3 absorption. [f] $J_{^{13}C-^1H} = 139$ Hz. [g] All samples in this table gave sharp absorption signals except this solution. In this solvent, $\omega^1/_2 \approx 65$ Hz. This is not due to impure compound since the same material in other solvents gave sharp signals. [h] $J_{^{13}C-^1H} = 141$ Hz. [i] Phenyl multiplet occurs at δ 6.9–7.5 ppm. (Area for CH_3)/(area for C_6H_5) = 1.13 (calculated ratio is 1.11). [j] Chemical shift of coordinated CH_3CN is 2.38 ppm. $J_{^{195}Pt-^1H} = 15$ Hz. [k] Chemical shift of coordinated CH_3CN is 2.45 ppm. $J_{^{195}Pt-^1H} = 15.4$ Hz. [l] Obscured by solvent.

$C_9H_{18}N_3BF_4 \cdot {}^1/_2H_2O$: C, 40.94; H, 7.25. Found: C, 40.88; H, 7.09. Uv (CH_3OH): ν_{max} 43.5 kK (ε 19,800).

$[R_3C_3]_2[Pt_2Cl_6]$ [R = $(CH_3)_2N$ (I) or $n\text{-}C_3H_7$ (II)]. These were prepared in similar ways so only one preparation will be described. A 0.40-g (0.97-mmol) sample of K_2PtCl_4 and 0.25 g (0.99 mmol) of $[(n\text{-}C_3H_7)_3C_3][BF_4]$ were dissolved in 8 ml of deoxygenated H_2O under N_2. (N_2 atmospheres were used routinely but they are probably not necessary.) The red solution deposited an orange-pink precipitate during 2.2 hr of stirring at 60°. Prolonged reaction times did not increase the yield and did cause decomposition of the product. The solution was filtered in the atmosphere and the product was washed with H_2O. Yields varied from 55 to 78%. Compound II was crystallized from acetone, in which it is very soluble, to give long pink needles, mp 149–150°. It is also very soluble in CH_2Cl_2, moderately soluble in CH_3OH and EPA [5:5:2 (vol/vol/vol) ether-isopentane-ethanol], and insoluble in cyclohexane. Compound I was crystallized from acetone, in which it is somewhat soluble, or CH_2Cl_2-acetone, in which it is more soluble. The product crystallized as pink to brick red needles or prisms, mp 190° dec. The pink and red crystals exhibited identical ir and uv-vis spectra in KBr pellets. Both compounds and their solutions are air stable, though they solvolyze overnight in acetone at room temperature. *Anal.* Calcd for $C_{24}H_{42}Pt_2Cl_6$: C, 30.88; H, 4.54; Pt, 41.80; Cl, 22.79. Found: C, 30.75; H, 4.64; Pt, 41.59, Cl, 22.79. Calcd for $C_{18}H_{36}N_6Pt_2Cl_6$: C, 23.01; H, 3.86; Pt, 41.53; Cl, 22.64. Found: C, 23.07; H, 3.87; Pt, 41.70; Cl, 22.64.

$[R_3C_3]_2[Pd_2Cl_6]$ [R = $(CH_3)_2N$ (III) or $n\text{-}C_3H_7$ (IV)]. Both compounds were prepared similarly. A 0.45-g (1.7-mmol) sample of $\{[(CH_3)_2N]_3C_3\}\{BF_4\} \cdot {}^1/_2H_2O$ in 10 ml of H_2O was added to a solution of 0.50 g (1.7 mmol) of Na_2PdCl_4 in 10 ml of H_2O with vigorous magnetic stirring. After 5 min the orange-pink precipitate was filtered, washed with H_2O, and crystallized from CH_2Cl_2-acetone to give orange-red prisms, mp 232° dec. Compound IV was crystallized from acetone to give long, thin orange-pink needles, mp 105–106°. Yields ranged from 50 to 70%. Solubility properties and air stability are similar to the Pt analogs. *Anal.* Calcd for $C_{24}H_{42}Pd_2Cl_6$: C, 38.12; H, 5.60; Pd, 28.14; Cl, 28.13. Found: C, 38.10; H, 5.82; Pd, 27.39; Cl, 27.86. Calcd for $C_{18}H_{36}N_6Pd_2Cl_6$: C, 28.37; H, 4.76; Pd, 27.93; Cl, 27.91. Found: C, 27.96; H, 4.47; Pd, 27.94; Cl, 28.30.

$\{[(CH_3)_2N]_3C_3\}\{Cl\}$. An 0.85-g sample of $\{[(CH_3)_2N]_3C_3\}\{BF_4\} \cdot {}^1/_2H_2O$ in 10 ml of H_2O was passed through a column of 4 g of Mallinckrodt Amberlite IRA 400 anion-exchange resin loaded with KCl. The eluate was concentrated and passed a second time through a fresh anion-exchange column, which removed all traces of BF_4^- absorption from the ir spectrum of the hygroscopic white solid.

$[(n\text{-}C_3H_7)_3C_3][X]$ (X = Cl, Br). These oils, which could not be crystallized from H_2O, ethanol, CH_2Cl_2, or C_6H_6, were obtained by ion exchange in the manner described above.

$\{[(CH_3)_2N]_3C_3\}\{B(C_6H_5)_4\}$. An 0.08 g sample of $\{[(CH_3)_2N]_3C_3\}\{BF_4\} \cdot {}^1/_2H_2O$ in 2 ml of H_2O was added to a filtered solution of 0.12 g of $NaB(C_6H_5)_4$ in 4 ml of H_2O with vigorous magnetic stirring. The voluminous white precipitate was filtered, washed with water, and crystallized from acetone–ether; mp 187–188°.

$\{[(CH_3)_2N]_3C_3\}\{(CH_3CN)PtCl_3\}$. Compound I was dissolved in CH_3CN to produce a nearly saturated solution after 1 hr of stirring at room temperature. The solution was filtered and allowed to stand 1–3 days with a loose cap until orange crystals began to form. (Seed crystals may be obtained by precipitating a small quantity of solution with hydrocarbon.) Crystallization was continued for 1 day at 0° and 1 day at −20°; mp 164°. *Anal.* Calcd for $C_{11}H_{21}N_4PtCl_3$: C, 25.85; H, 4.14; Pt, 38.17; Cl, 20.81. Found: C, 25.93; H, 3.99; Pt, 39.22; Cl, 20.80. Ir (KBr pellet, 2000–300 cm^{-1}): 1810 (vw), 1764 (vw), 1640 (sh, w), 1550 (br, vs), 1444 (w), 1415 (m), 1400 (s), 1282 (vw), 1221 (m), 1132 (w), 1052 (w), 1026 (m), 958 (vw), 784 (m), 618 (vw), 588 (vw), 344 (m), 328 (m), 316 (sh, w) cm^{-1}.

$\{[(CH_3)_2N]_3C_3\}_2\{PtCl_4\}$. A 190-mg (0.20-mmol) sample of I in 2 ml of CH_2Cl_2 was treated with 47 μl (0.40 mmol) of $P(OCH_3)_3$. After 3.5 hr of stirring at 25°, 2.5 ml of acetone was added to reduce the solubility of the products and the solution was left overnight at −20°. (Addition of acetone may initiate some precipitation.) Large red needles of starting material (identified by its ir spectrum) were picked out of the pink microcrystalline product which was washed with ether and dried *in vacuo*. This pink powder (mp 218° dec) was identified spectroscopically as $\{[(CH_3)_2N]_3C_3\}\{PtCl_4\}$. Uv ($CH_2Cl_2$): ~17.0 kK (sh) (ε 5.5), 20.00 kK (16.9), 24.77 kK (53.2), 29.24 kK (67.0). (See supplementary Table I for the spectrum of $[(n\text{-}C_4H_9)_4N]_2[PtCl_4]$.[9]) Ir (KBr pellet, 400–280 cm^{-1}): 315 cm^{-1}. Raman (solid, 400–280 cm^{-1}): 328, 306 cm^{-1}. Nmr (CH_2Cl_2): δ 3.25 ppm (singlet). Presumably the other reaction product is $[(CH_3O)_3P]_2PtCl_2$.

Results and Discussion

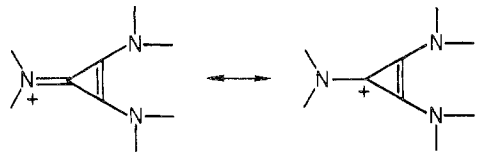
Synthesis and Structure. The salts $[R_3C_3]_2[M_2Cl_6]$ (I–IV) precipitate from aqueous solutions of $R_3C_3^+$ and MCl_4^{2-}.

(9) See paragraph at end of paper regarding supplementary material.

When M = Pd, precipitation is immediate upon mixing the solutions at room temperature. When M = Pt, heating to 60° for 2.2 hr is necessary to effect product formation. A crystallographic study of compound I has established[10] that the $Pt_2Cl_6^{2-}$ unit is sandwiched between parallel $R_3C_3^+$ ions in the arrangement shown in Figure 1. The distance from a Pt atom to the plane of its adjacent $R_3C_3^+$ cation is about 4 Å. Polarized electronic spectral measurements on single crystals of I at 5°K have shown[10] that the transitions attributable to $Pt_2Cl_6^{2-}$ are not perturbed significantly by $R_3C_3^+$, which suggests that specific d-orbital interactions with the cation are relatively unimportant.

The ^{1}H nmr spectra of I-IV in several solvents (Table I) indicate the presence of three equivalent R groups. The chemical shifts of the cyclopropenium α-CH_2 or *N*-CH_3 protons when the anion is $M_2Cl_6^{2-}$ are consistently 0.1-0.5 ppm downfield of the chemical shifts found in solutions containing other anions, in agreement with expectation for 1:2 electrolytes exhibiting partial ion pairing. The absence of coupling to ^{195}Pt rules against any appreciable covalent character in the ion-pair bonds in solution.[11] Electronic spectra and molar conductances in solution for I-IV are reported in supplementary Tables I and II, respectively.[9]

All of the infrared absorption bands of the cyclopropenium salts in the region 350-3000 cm^{-1} which are not due to BF_4^- [12] are essentially anion independent (supplementary Tables III and IV[9]). If compounds I-IV were π-cyclopropenium complexes, one would expect a marked decrease in the energies of the degenerate cyclopropenium "ring breathing" mode, ν_d(C⋯C).[13,14] This absorption has been assigned[15] in the region 1380-1430 cm^{-1} for several cyclopropenium salts. The only band in this region in the spectrum of $(n\text{-}C_3H_7)_3C_3^+$, as the BF_4^- or $M_2Cl_6^{2-}$ salts, occurs at 1383 ± 2 cm^{-1}. As we expect a methyl C-H bending vibration at this frequency, either the two types of vibrations are essentially degenerate or the 1383-cm^{-1} band does not contain ν_d(C⋯C). An intense band at 1560 cm^{-1} in the spectrum of $[(CH_3)_2N]_3C_3^+$ is assigned as the degenerate, asymmetric C⋯N stretch, the high frequency of which attests to the importance of resonance structures of type A.



A B

The far-infrared paraffin pellet spectra of compounds I-IV, and corresponding tetraphenylarsonium salts,[16] are shown in Figure 2.[17] Because of the very high sample concentrations used for these spectra, many of the intense bands above 300 cm^{-1} are off scale. The point of showing these spectra is that the sharp, medium-intensity band near 190 cm^{-1}, assigned as a fundamental of $Pd_2Cl_6^{2-}$ by Adams, *et al.*,[16] is definitely attributable to the tetraphenylarsonium cation. A replacement for this fundamental is not obvious, but it is possible that the weak bands near 230 cm^{-1}, observed in the spectra of all of the salts of $Pd_2Cl_6^{2-}$ and $Pt_2Cl_6^{2-}$, might be due to the terminal MCl_2 bending vibration.[18]

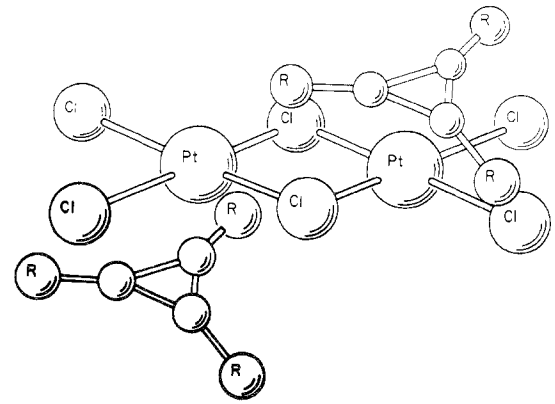


Figure 1. The arrangement of cyclopropenium cations and $Pt_2Cl_6^{2-}$ anions in a crystal of I. The $R_3C_3^+$ cations are stacked above and below the plane of the anion, each cation being near one of the Pt atoms. The platinum-cyclopropenium distance is about 4 Å.[10]

Cleavage Reactions. Solutions of $Pt_2Cl_6^{2-}$ in acetonitrile turn from pink to yellow in the course of about 1 hr as the product is formed. Solutions of $Pd_2Cl_6^{2-}$ are at equilibrium upon dissolution in acetonitrile. A spectrophotometric titration in which IV was treated with 0, 47.6, and 1060 equiv of CH_3CN showed an isosbestic point at 416 nm and gave an equilibrium constant for reaction 4 of 5×10^{-2} l. mol^{-1}

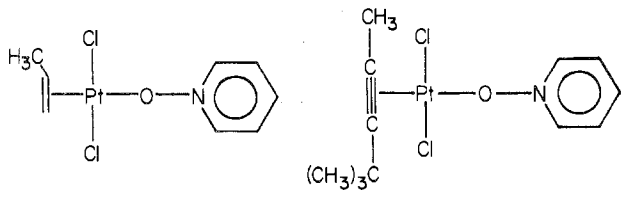
$$Pd_2Cl_6^{2-} + 2(CH_3CN) \overset{K_4}{\rightleftharpoons} 2(CH_3CN)PdCl_3^- \quad (4)$$

21°. In contrast, the observation that the nmr spectrum of $(CH_3CN)PtCl_3^-$ (as the $[(CH_3)_2N]_3C_3^+$ salt) in CH_2Cl_2 shows no free CH_3CN allows us to state that $K_4 > 10^4$ l. mol^{-1} when M = Pt. That one molecule of CH_3CN per Pt atom is taken up can be shown unequivocally by comparing the areas of the signals of coordinated CH_3CN and cyclopropenium cations in the proton nmr spectra (Table I). The coordinated CH_3CN gives a signal about 0.4 ppm downfield of free CH_3CN ($J_{^{195}Pt-^1H} \approx 15$ Hz). Elemental analysis of a sample of pure crystalline $\{[(CH_3)_2N_3]C_3\}\{(CH_3CN)PtCl_3\}$ also confirms this stoichiometry.

The Raman spectrum indicates an N-bonded CH_3CN, as

(10) The crystal structure of I has been determined by J. Thibeault and R. Ziolo, unpublished results.

(11) In the compounds i and ii $^3J_{^{195}Pt-C-C-^1H} = 40.5$ and 29.0



i ii

Hz, respectively: P. D. Kaplan and M. Orchin, *Inorg. Chem.*, 6, 1096 (1967). We would anticipate a coupling constant in this range between ^{195}Pt and the α-CH_2 protons of II, had a π complex been formed.

(12) K. O. Christe and W. Sawodny, *Inorg. Chem.*, 8, 212 (1969).

(13) H. P. Fritz, *Advan. Organometal. Chem.*, 1, 239 (1964).

(14) In the Ph.D. thesis of R. M. Tuggle (Carnegie-Mellon University, 1971), ν_d(C⋯C) of the π-cyclopropenium ligand in $[\pi\text{-}C_3(C_6H_5)_3]NiCl(C_5H_5N)_2 \cdot C_5H_5N$[1b] is tentatively assigned at either 1370 or 1350 cm^{-1}. This is shifted *ca.* 50 cm^{-1} from the value of 1425-1400 cm^{-1} found for the free cation, $(C_6H_5)_3C_3^+$. We thank Dr. D. L. Weaver for this information.

(15) G. L. Closs, *Advan. Alicyclic Chem.*, 1, 53 (1966).

(16) D. M. Adams, P. J. Chandler, and R. G. Churchill, *J. Chem. Soc. A.*, 1272 (1967).

(17) $Pd_2Cl_6^{2-}$ reacts with several pelleting agents. This is evidenced by the appearance of Pd-Br stretching absorptions near 260 cm^{-1} in KBr and TlBr pellets and a striking color change in CsI. The $Pt_2Cl_6^{2-}$ salts and the tetraphenylarsonium salt of $Pd_2Cl_6^{2-}$ do not appear to react with KBr.

(18) We have derived the entire *G* matrix for in-plane and out-of-plane vibrations of $M_2Y_2X_4$ molecules of D_{2h} symmetry. This includes some corrections to the partial *G* matrix published previously.[16] The entire *G* matrix is given in the microfilm edition of this journal.[9]

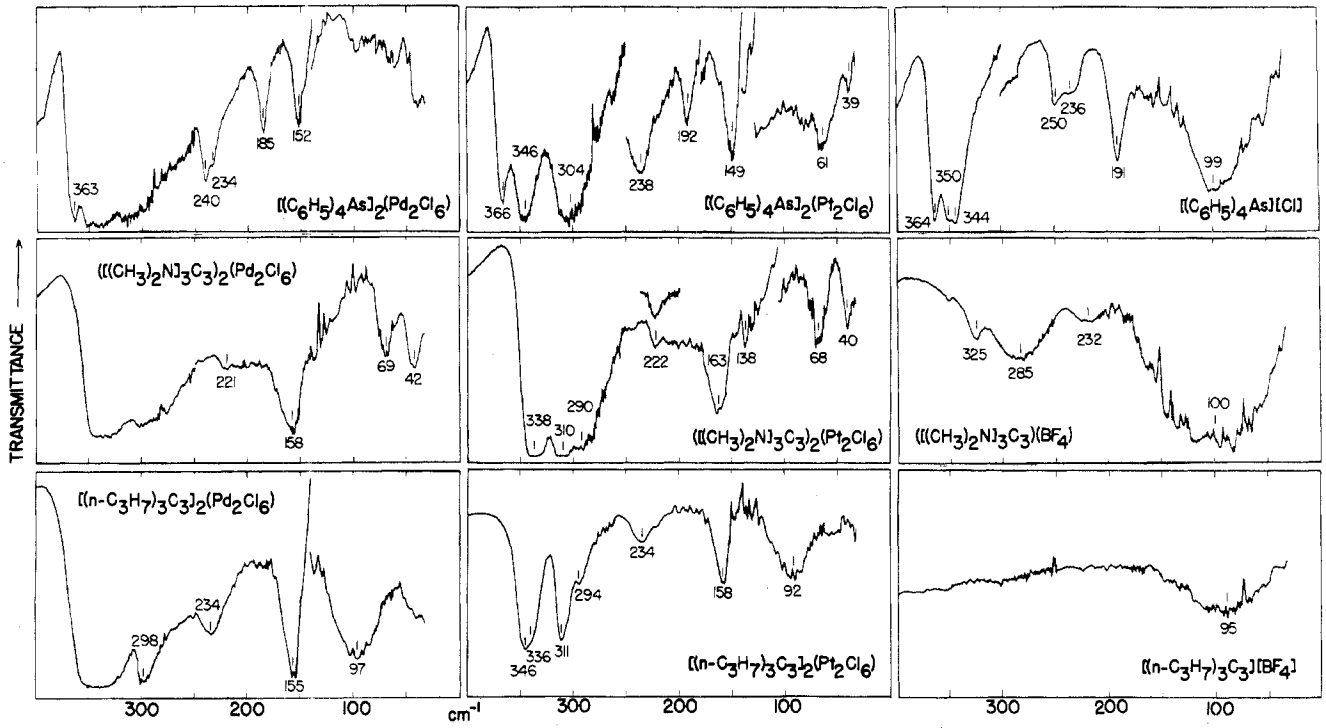


Figure 2. Paraffin pellet far-infrared spectra (400-33 cm^{-1}) of a series of $M_2Cl_6^{2-}$ salts (M = Pt, Pd). Cation spectra are given on the right for comparison.

Table II. Infrared and Raman Spectra of $(CH_3CN)MCl_3^-$ Salts in CH_3CN (cm^{-1})

Cation	Metal	Cell[b]	ν_s(Cl-M-Cl)(a_1)	ν_{as}(Cl-M-Cl)(b_1)	ν(M-Cl_{trans})(a_1)
			Infrared[a]		
$(n\text{-}C_3H_7)_3C_3^+$	Pt	CsI	347 m	330 s	~319 sh, w
$[(CH_3)_2N]_3C_3^+$	Pt	CsI	345 m	330 s	~317 sh, w
$[(CH_3)_2N]_3C_3^+$	Pt	AgCl	~344 br, w	328 br, m	~316 sh, w
$(n\text{-}C_3H_7)_3C_3^+$	Pd	AgCl		340 s	302 vw
$[(CH_3)_2N]_3C_3^+$	Pd	AgCl		339 s	~300 vw
			Raman[c]		
$(n\text{-}C_3H_7)_3C_3^+$	Pt		347 (0.44)		324 (1.00)
$[(CH_3)_2N]_3C_3^+$	Pt		346 (0.28)		325 (1.00)
$(n\text{-}C_3H_7)_3C_3^+$	Pd		348 (0.34)		302 (1.00)
$[(CH_3)_2N]_3C_3^+$	Pd		346 (0.31)		301 (1.00)

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad; ν_s, symmetric stretch; ν_{as}, asymmetric stretch. [b] It is necessary to specify the type of cell since solutions of $Pd_2Cl_6^{2-}$ react immediately with CsI cells. Several platinum halides have been observed to react with common infrared cell materials. See L. Spaulding, B. A. Reinhardt, and M. Orchin, *Inorg. Chem.*, **11**, 2092 (1972). [c] The numbers in parentheses are the relative integrated intensities of the two peaks in each spectrum. All bands are polarized. All measurements were done using glass capillary tubes as cells.

opposed to a π-bonded ligand, as ν(CN) shifts to higher energy than that of free CH_3CN upon N-coordination to a metal.[19,20] Free CH_3CN exhibits ν(CN) at 2253 cm^{-1} and a much weaker combination band at 2294 cm^{-1}.[21] In addition, solutions of $(CH_3CN)PtCl_3^-$ show two weak bands at 2306 and 2336 cm^{-1} attributable to coordinated CH_3CN (Figure 3).

The Raman and infrared spectra (Table II) support the assumed C_{2v} square-planar geometry of $(CH_3CN)MCl_3^-$. The three M-Cl stretching vibrations transform as 2 a_1 [ν(M-Cl_{trans}) and ν_s(Cl-M-Cl)] + b_1 [ν_{as}(Cl-M-Cl)] and all are both infrared and Raman active. It is commonly found that ν_{as} is the strongest band in the infrared spectrum. For all these salts we observe a strong band in the infrared spectrum in the region 328-340 cm^{-1}, as well as one or two weaker bands. Corresponding to these weak infrared bands are strong Raman bands. No Raman absorption occurs at the frequency of the strong infrared absorption. We assign ν_{as}(b_1) as the strong infrared band and ν_s(Cl-M-Cl)(a_1) and ν(M-Cl_{trans})(a_1) as the two Raman bands. Spaulding, *et al.*,[21,22] have cited nmr evidence which indicates that CH_3CN has a greater trans influence than Cl^-. Hence we assign ν(M-Cl_{trans}) at lower frequency than ν_s(Cl-M-Cl) by analogy to the assignment of $(\pi\text{-}C_2H_4)PtCl_3^-$.[23,24]

Reaction of I or II with cyclooctene (C_8H_{14}) in CH_2Cl_2 requires about 3-6 hr to reach equilibrium at room temperature. The visible absorption spectrum of pure $Pt_2Cl_6^{2-}$ in CH_2Cl_2 (exposed to the air) changes somewhat during this

(19) R. A. Walton, *Quart. Rev., Chem. Soc.*, 19, 126 (1965).
(20) A π-CH_3CN group would exhibit ν(CN) *ca.* 200 cm^{-1} *lower* than free CH_3CN: M. F. Farona and K. F. Kraus, *Inorg. Chem.*, 9, 1700 (1970).
(21) T. Weil, L. Spaulding, and M. Orchin, *J. Coord. Chem.*, 1, 25 (1971).
(22) L. Spaulding, B. A. Reinhardt, and M. Orchin, *Inorg. Chem.*, 11, 2092 (1972).
(23) M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, 88, 5454 (1966).
(24) Electronic spectra of the acetonitrile complexes are given in supplementary Table V.[9]

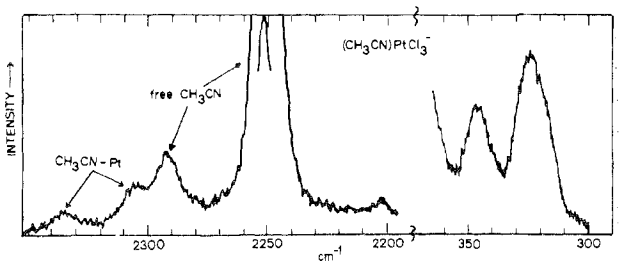


Figure 3. Raman spectrum of the C≡N and Pt—Cl stretching regions of $[(n\text{-}C_3H_7)_3C_3][(CH_3CN)PtCl_3]$ in CH_3CN solution. Bands labeled "free CH_3CN" are due to solvent.

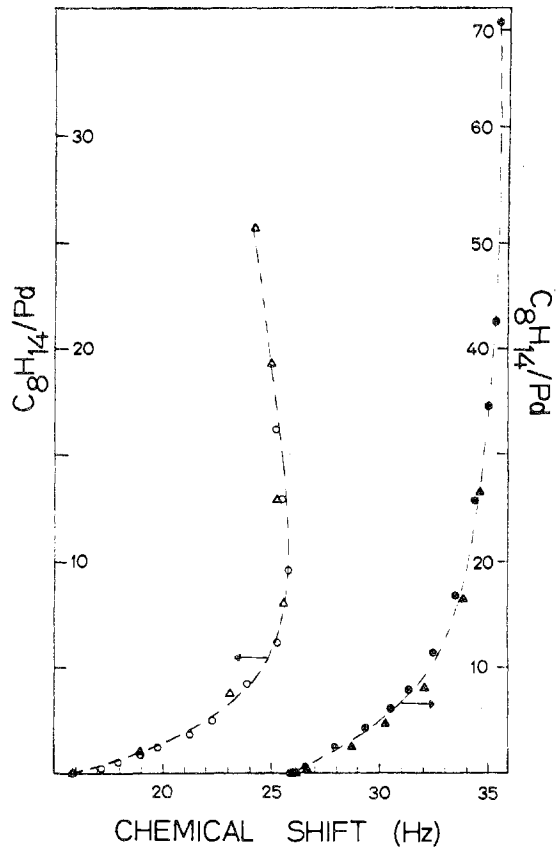


Figure 4. Chemical shift changes which occur when cyclooctene is added to solutions of III (right) and IV (left) in CH_2Cl_2. The chemical shifts are for the CH_3 protons of III and the α-CH_2 protons of IV. Shifts are measured in hertz upfield of the high-field $^{13}CH_2Cl_2$ satellite: ●, experiment I, supplementary Table VI; ▲, experiment II, supplementary Table VI; ○, experiment I, supplementary Table VII; △, experiment II, supplementary Table VII.

time span so we were unable to do an accurate spectrophotometric titration of $Pt_2Cl_6^{2-}$ with cyclooctene. Nonetheless, changes in the spectrum of $Pt_2Cl_6^{2-}$ in the presence of cyclooctene are linear in added cyclooctene and halt abruptly at C_8H_{14}:Pt = 1.0. This indicates quantitative uptake of cyclooctene by $Pt_2Cl_6^{2-}$ and we can estimate that $K_5 > 4 \times$

$$Pt_2Cl_6^{2-} + 2C_8H_{14} \overset{K_5}{\rightleftharpoons} 2(C_8H_{14})PtCl_3^- \quad (5)$$

10^5 l. mol^{-1} at 21°. The resulting yellow solutions show only a shoulder at ~22 kK (ε ~20) in the range 750-360 nm, which is consistent with an (olefin)$PtCl_3^-$ structure.[25,26]

Reaction of $Pd_2Cl_6^{2-}$ with cyclooctene in CH_2Cl_2 occurs

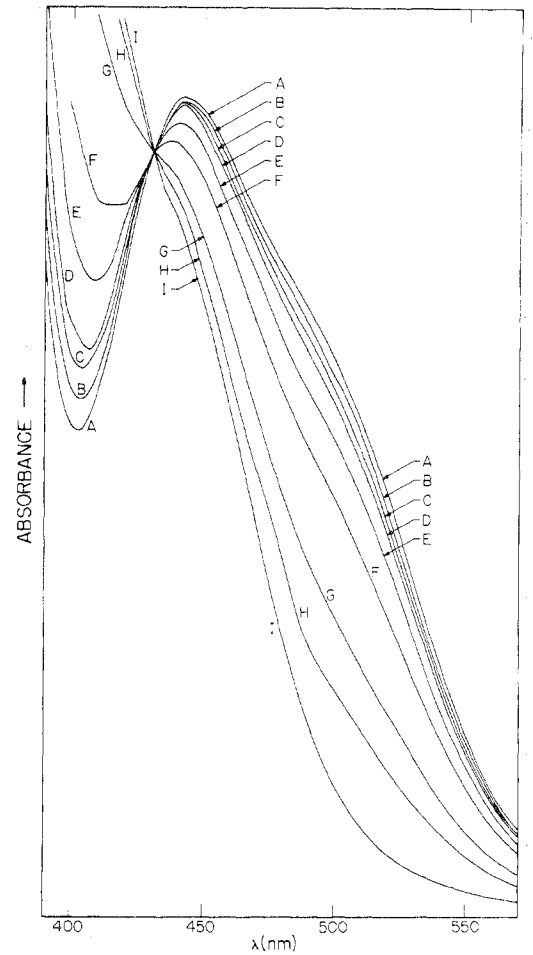


Figure 5. Spectrophotometric titration of III with cyclooctene in CH_2Cl_2. $[C_8H_{14}]/[Pd]$ ratio for each curve is (A) 0, (B) 0.899, (C) 1.80, (D) 2.70, (E) 5.62, (F) 11.2, (G) 29.0, (H) 45.0, and (I) 687. An isosbestic point is maintained at 430 nm.

within the time of mixing reagents. When the counterion is $[(CH_3)_2N]_3C_3^+$, the reaction proceeds smoothly to form $(C_8H_{14})PdCl_3^-$ (eq 6). The reaction of III with cyclo-

$$Pd_2Cl_6^{2-} + 2C_8H_{14} \overset{K_6}{\rightleftharpoons} 2(C_8H_{14})PdCl_3^- \quad (6)$$

octene can be followed by the change in the nmr chemical shift of the cyclopropenium CH_3 protons (Figure 4) and by the change in the electronic absorption spectrum (Figure 5). The method used to extract K_6 from these titrations is described in the microfilm edition of this journal.[9] The results are K_6 = 2.7 l. mol^{-1} at 21° (visible spectra) and 0.7 l. mol^{-1} at about 40° (nmr). Both the lower stabilities of the olefin-palladium as compared to the olefin-platinum complexes and the faster rates of the Pd cleavage reactions are consistent with established trends.[4,5,27] The spectrum of $(C_8H_{14})PdCl_3^-$ in the region 750-290 nm exhibits a shoulder at 23 kK (ε 300) and a peak at 31.5 kK (ε 4500).

In marked constrast to III, reaction of IV with cyclooctene occurs in at least two discrete steps. This is most obvious from the changes in the visible absorption spectrum (Figure 6). An isosbestic point at 462 nm is preserved through addition of the first 1.6 equiv of cyclooctene. As further olefin is added, the isosbestic point disappears and the spectrum eventually resembles that of the product of the reaction of C_8H_{14} with III (Figure 5). The nmr spectrum (Figure 4) is

(25) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1322 (1967).
(26) J. W. Moore, *Acta Chem. Scand.*, 20, 1154 (1966).
(27) F. R. Hartley, *Chem. Rev.*, 69, 799 (1969).

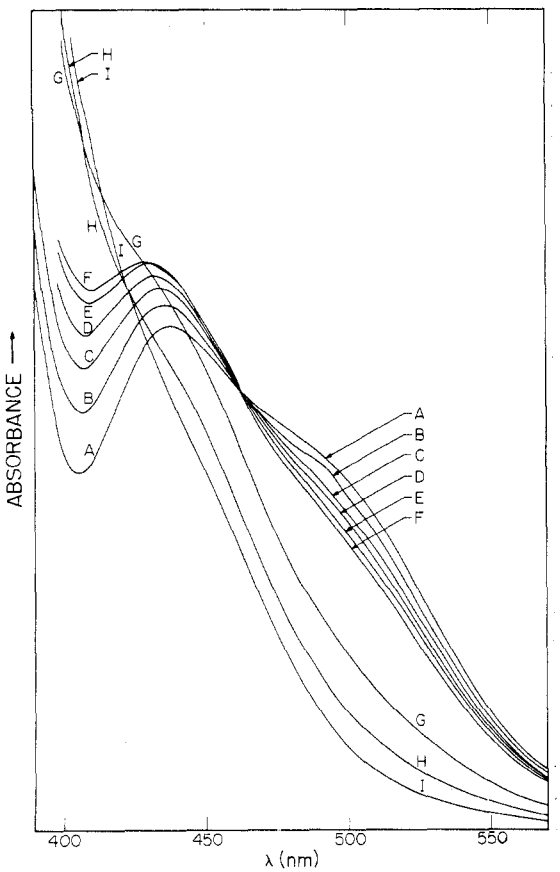
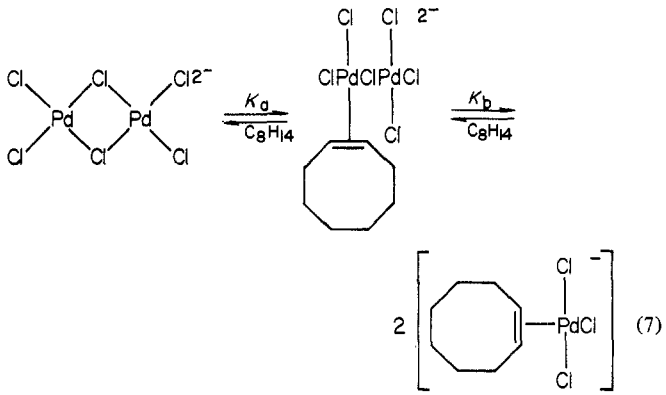


Figure 6. Spectrophotometric titration of IV with cyclooctene in CH_2Cl_2. $[C_8H_{14}]/[Pd]$ ratio for each curve is (A) 0, (B) 0.404, (C) 0.808, (D) 1.21, (E) 1.62, (F) 2.02, (G) 10.1, (H) 20.2, and (I) 262. The isosbestic point at 462 nm is maintained only for curves A–E.

consistent with a two-step reaction as the chemical shift of the cyclopropenium α-CH_2 protons first proceeds upfield as olefin is added and then moves back downfield.

Both spectroscopic data and kinetic considerations[4,5] suggest reaction scheme 7. The assigned structure of the intermediate is supported by spectrum E in Figure 6, which shows that the first two $PdCl_4^{2-}$ absorptions in the region 400–500 nm are clearly preserved. We suggest that a "sandwich" structure similar to that shown in Figure 1 in which the flat $(n\text{-}C_3H_7)_3C_3^+$ cation binds specifically to the planar anion is responsible for the stabilization of the proposed monochloro-bridged intermediate. The observed difference in the behavior of the two different cyclopropenium cations is remarkable. The stabilization of the intermediate accord-



ing to this model is provided by weak coordination to the $(n\text{-}C_3H_7)_3C_3^+$ group, perhaps in a π-type interaction. The absence of such weak coordination in the case of $[N(CH_3)_2]_3C_3^+$ is not unreasonable, as Kerber and Hsu have shown that cyclopropenium cation stabilization is substantially greater for R_2N than for alkyl substituents.[28] The highly stabilized $[N(CH_3)_2]_3C_3^+$ cation would not be expected to profit as much from weak metal-ring interaction as would $(n\text{-}C_3H_7)_3C_3^+$.

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Registry No. I, 51446-43-6; II, 51446-44-7; III, 51446-45-8; IV, 51446-46-9; $[(n\text{-}C_3H_7)_3C_3][BF_4]$, 51391-83-4; $\{[(CH_3)_2N]_3C_3\}\{BF_4\}$, 51391-89-0; $\{[(CH_3)_2N]_3C_3\}\{Cl\}$, 51391-90-3; $[(n\text{-}C_3H_7)_3C_3][Cl]$, 51391-84-5; $[(n\text{-}C_3H_7)_3C_3][Br]$, 51464-60-9; $\{[(CH_3)_2N]_3C_3\}\{B(C_6H_5)_4\}$, 51391-91-4; $\{[(CH_3)_2N]_3C_3\}\{(CH_3CN)PtCl_3\}$, 51319-93-6; $\{[(CH_3)_2N]_3C_3\}_2\{PtCl_4\}$, 51391-92-5; $[(n\text{-}C_3H_7)_3C_3][(CH_3CN)PtCl_3]$, 51391-86-7; $[(n\text{-}C_3H_7)_3C_3][(CH_3CN)PdCl_3]$, 51391-88-9; $\{[(CH_3)_2N]_3C_3\}\{(CH_3CN)PdCl_3\}$, 51391-94-7; K_2PtCl_4, 10025-99-7; Na_2PdCl_4, 13820-53-6; CH_3CN, 75-05-8; C_8H_{14}, 931-88-4; $(C_8H_{14})Cl_2Pd\text{-}Cl\text{-}PdCl_3^{2-}$, 51464-61-0.

Supplementary Material Available. Supplementary tables and discussion will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036 Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2250.

(28) R. C. Kerber and C.-M. Hsu, *J. Amer. Chem. Soc.*, **95**, 3239 (1973).