

Each of these reactions is accompanied by the displacement of a tolyl group, and in the reactions involving the triphenylphosphine and pyridine derivatives the addition of methyl iodide yields a platinum(IV) com-

pound. The isolation of VI, in which the platinum has an oxidation number of +2, indicated that these reactions may proceed *via* displacement and subsequent addition of methyl iodide in the presence of the bulky *o*-tolyl group.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WAYNE STATE UNIVERSITY, DETROIT 2, MICHIGAN

Nuclear Magnetic Resonance Spectra and Stereochemistry of Propenylmercury Compounds^{1,2}

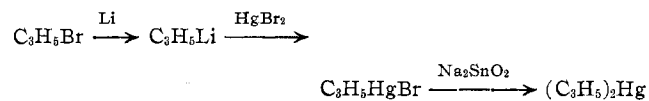
BY D. MOY, M. EMERSON, AND J. P. OLIVER

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The coupling constants and chemical shifts have been determined from the n.m.r. spectra of di-(*cis*-, *trans*-, and *iso*-)-propenylmercury. These values and the Hg¹⁹⁹-H coupling have been used to determine the absolute configurations of these compounds.

Introduction

Nesmeyanov³ has synthesized isomers of propenylmercuric bromide and dipropenylmercury by the series of reactions



He proposed that this series of reactions takes place with complete retention of configuration and has further demonstrated this by a series of metal exchange reactions making use of "odd and even cycles." This conclusion is further substantiated by the proof of the structure of *trans*- β -chlorovinylmercuric chloride from X-ray crystal data⁴ and its similarity in reactions to the propenyl derivatives. Dipole moment studies on the organomercuric chlorides were consistent with the stereochemical assignments as were the melting points of all of the derivatives and their infrared spectra. However, the data presented are only indirect proof of isomeric purity since the chemical analysis, melting points, and dipole moments would still be consistent with isomeric mixtures. To date, only the reaction of lithium metal with the propenyl halides has been shown to proceed with complete retention of geometry by direct spectroscopic evidence.⁵

The n.m.r. spectra of these compounds would allow the direct determination of the isomeric form present as well as detect the presence of mixtures of isomers or other impurities. The determination of the magnitude of the proton spin-spin coupling constants allows one to assign the relative steric relationships of the hydrogen atoms to one another since it has been well established⁶ that $J_{trans} > J_{cis} > J_{gem}$. This relationship has been substantiated by a valence bond calculation of the vinyl coupling constants by Karplus.⁷ The *trans* coupling constants have been shown to take on values from 14 to 20 c.p.s., the *cis* from 5-15 c.p.s., and the *gem* from 0-5 c.p.s.

Naturally occurring mercury is made up of several isotopes, one of which, Hg¹⁹⁹, possesses a spin of $I = 1/2$ and is present in a natural abundance of 17%. The mercury spin can couple with the proton spins and give rise to satellite peaks in the proton resonance spectrum. It has been observed that the Hg¹⁹⁹-H coupling constants in divinylmercury⁸ follow the order $J_{trans} > J_{cis} > J_{gem}$. Since one would expect that the substitution of a methyl group would not change this order, the magnitudes of these Hg¹⁹⁹-H couplings can be used to confirm the structural assignments of the propenyl groups.

Experimental

The syntheses of the dipropenylmercury derivatives starting from propenyl bromide were accomplished through the above series of reactions described by Nesmeyanov.³

(1) This work was supported in part by the National Science Foundation, Grant NSF-G-15829.

(2) Based upon a thesis submitted by David Moy in partial fulfillment of the requirements for the Doctor of Philosophy degree.

(3) A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1174 (1959) (English translation).

(4) A. I. Kitaigorodsky, *ibid.*, 170 (1945); *ibid.*, 259 (1947).

(5) N. L. Allinger and R. B. Hermann, *J. Org. Chem.*, **26**, 1040 (1961).

(6) T. Schaeffer, *Can. J. Chem.*, **40**, 1 (1962).

(7) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(8) D. W. Moore and J. A. Happe, *J. Phys. Chem.*, **65**, 224 (1961).

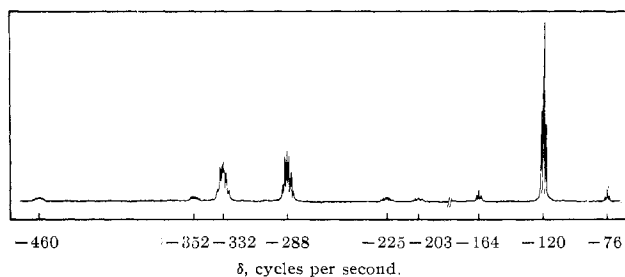


Fig. 1.—The nuclear magnetic resonance spectrum of diisopropenylmercury. The methyl and vinyl regions were recorded at different gain settings.

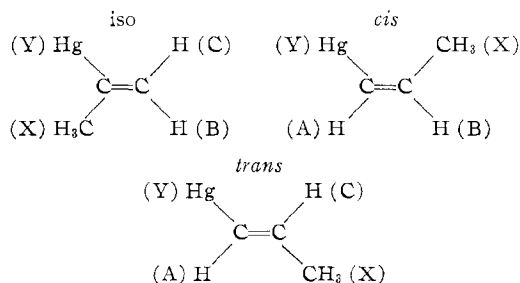
All of the dipropenylmercury compounds were purified by repeated vacuum distillations and were transferred directly into the n.m.r. sample tubes, along with the solvent and internal standard (tetramethylsilane, TMS), by distillation from the vacuum system.

All n.m.r. samples were made up to approximately 10–20% concentration in carbon tetrachloride. The spectra were run on a Varian HR 60 nuclear magnetic resonance spectrometer. Line positions were obtained by a linear interpolation between TMS side bands. The audio side band frequencies were measured to ± 1 part in 10^5 using a H-P 523 CR counter operating in the period count mode with a 1 Mc. clock. The average error in line positions was ± 0.2 c.p.s. for the parent peaks and ± 0.5 c.p.s. for the less well resolved satellite lines.

N.m.r. Spectra and Interpretations

The n.m.r. spectra of the three dipropenylmercury derivatives obtained from *iso*-, *cis*-, and *trans*-propenyllithium are shown, respectively, in Fig. 1, 2, and 3. These all show the characteristic spectra of an ABX_3 system.⁹ First-order perturbation rules combined with the well known solution of the AB system¹⁰ were used to analyze the spectra. The presence of mercury satellites (especially apparent about the intense methyl peaks) with total intensities of 17% of that of the parent peaks indicates the formation of mercury compounds.

To simplify the discussion, the following identification of protons has been made.



Three main peaks are observed (Fig. 1) for the compound obtained from isopropenyllithium. Four Hg^{199} satellite peaks are associated with the two vinyl protons. The peaks at -7.667 and -3.391 p.p.m. are equally spaced around the vinyl peak at -5.532 p.p.m. The Hg^{199} -H splitting is 256.5 c.p.s. The satellites at

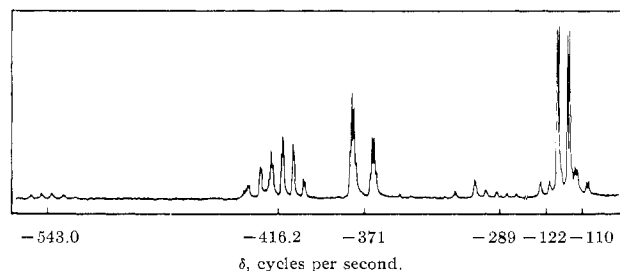


Fig. 2.—The nuclear magnetic resonance spectrum of di-*cis*-propenylmercury. The methyl and vinyl regions were recorded at different gain settings.

-5.874 and -3.744 p.p.m. are symmetrically located around the vinyl peak at -4.838 p.p.m. and the corresponding splitting is 127.8 c.p.s. The large Hg^{199} -H splitting of the low field peak indicates that this proton is *trans* to the mercury atom and, therefore, is assigned as the B proton.

The two vinyl proton peaks can be interpreted as consisting of sets of two superimposed quadruplets separated by the J_{BC} coupling of 4.1 c.p.s. The lines making up the quadruplets are separated by approximately 1.4 c.p.s., indicating that $J_{BX} \approx J_{CX} = 1.4$ c.p.s. This is also indicated by the fact that the methyl peak is a triplet. The J_{BX} and J_{CX} couplings are expected to be small since the coupling interaction extends over three carbon atoms. Therefore a value of 1.4 c.p.s. is very reasonable. The value of $J_{BC} = 4.1$ c.p.s. is of the correct magnitude for the coupling between geminal protons and hence unambiguously justifies the *iso* configuration assignment.

The n.m.r. spectrum of the product obtained from *cis*-propenyllithium is shown in Fig. 2. The methyl resonance appears as two doublets centered at -1.933 p.p.m. from TMS. Mercury satellites appear centered at 6 c.p.s. on either side of the center of the parent peaks. The small Hg^{199} -H coupling of $J_{XY} = 12$ c.p.s. indicates the mercury atom and the methyl group are on opposite ends of the molecule. The low field vinyl multiplet consists of two overlapping quadruplets giving rise to a hextuplet, centered at -6.932 p.p.m. The high field vinyl consists of the other two members of the AB doublet centered at -6.183 p.p.m. Each line of the doublet is further split into a quadruplet by the methyl protons. The low field multiplet was assigned as the B proton which is consistent with a vicinal coupling constant $J_{BX} = 6.5$ c.p.s. between the methyl and vinyl proton attached to the same carbon. The high field vinyl proton was assigned as proton A, which is consistent with $J_{AX} = 1.3$ c.p.s., indicating coupling over three carbon atoms. The coupling constant $J_{AB} = 11.1$ c.p.s. is reasonable for *cis* protons.

A hextuplet satellite is found centered at 122 c.p.s. on either side of the B proton multiplet giving $J_{BY} = 244$ c.p.s., which is the same order as the *trans* Hg^{199} -H coupling in diisopropenylmercury. The lower satellite of the A proton falls under the lower end of the B proton multiplet and the high field satellite is superimposed on the high field satellite of the B proton, making pre-

(9) It is probably more correct to classify the diisopropenylmercury as an AMX_3 system since the difference in chemical shift between the two vinyl protons is ten times larger than the coupling constant.

(10) J. A. Pople, W. G. Schneider, and H. G. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, N. Y., 1959, pp. 120–123.

cise measurement of splitting very difficult. The *gem* $\text{Hg}^{199}\text{-H}$ coupling constant J_{AY} is approximately 134 c.p.s. or about the same magnitude as the *cis* $\text{Hg}^{199}\text{-H}$ coupling in the iso compound.

The spectrum of the compound obtained from *trans*-propenyllithium is shown in Fig. 3. The spectrum is consistent with *trans*-dipropenylmercury. The methyl multiplet is very similar to that of the *cis* compound. The low field vinyl proton peaks have the same chemical shift as that observed for the A proton of the *cis* compound. The high field vinyl proton is assigned as the C proton. The spin-spin coupling $J_{\text{AC}} = 19.2$ c.p.s. and is the correct magnitude for *trans* H-H coupling. The vicinal coupling between proton C and the X_3 methyl protons $J_{\text{CX}} = 5.0$ c.p.s., giving rise to a well resolved pair of quadruplets since J_{AC} is large enough to eliminate any overlap. The mercury satellites of the methyl multiplet must be to some extent obscured by the parent peaks since only half of the multiplet is observed on each side. Only the vinyl multiplets corresponding to the strong peaks of the vinyl parents are observed since the intensities of the weaker peaks do not exceed the signal-to-noise ratio of the spectrometer. The $\text{Hg}^{199}\text{-H}$ vinyl couplings are the correct magnitude for proton A *gem* to the mercury and proton C *cis* to the mercury atom.

Conclusions

In the above reactions of the three propenyllithium isomers to give the propenylmercuric bromides and then the dipropenylmercurys, the retention of configuration was complete. The n.m.r. spectra of the resulting isomers of dipropenylmercury show no evidence of isomerization. The final products were very nearly 100% pure, since only trace amounts of other proton-containing material is apparent from the n.m.r. spectra. Only slight variations in the spectra were observed for different samples. The maximum amount of impurities in any sample is estimated to be less than 5 proton %.

The coupling constants and chemical shifts for the dipropenylmercury isomers are summarized in Table I. Values for divinylmercury reported by Moore and Happe⁸ are included for comparison. The assigned coupling constants between vinyl protons of the dipropenylmercury isomers are very close to those of the divinylmercury. The coupling constants also agree very well with those of the three isomeric tripropenyl-gallium-trimethylamine adducts.¹¹ The coupling constants and chemical shifts of the *trans* isomer are somewhat in error since first-order perturbation rules were used in determining the values from the spectrum. Their application is not really justified since $J_{\text{AC}} \approx 0.5(\delta_{\text{A}} - \delta_{\text{C}})$, *i.e.*, the A and C protons are strongly coupled. The largest error, introduced in the values of δ_{A} and δ_{C} , may be as large as 0.02 p.p.m. The errors in the coupling constants will be only a few tenths of a cycle. The largest effect of the strong coupling is the

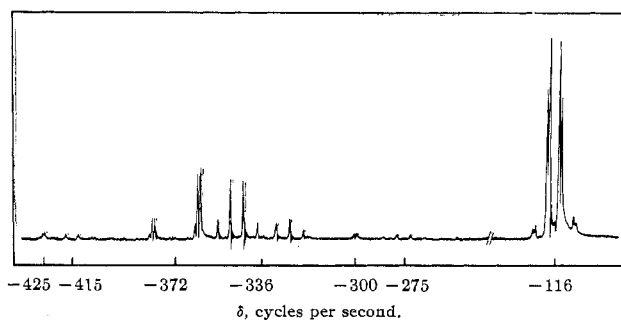


Fig. 3.—The nuclear magnetic resonance spectrum of di-*trans*-propenylmercury. The methyl and vinyl regions were recorded at different gain settings.

TABLE I
 δ_i AND J_{ij} FOR ISOMERS OF DIPROPENYL MERCURY AND DIVINYLMERCURY

	Diiso-propenylmercury ^a	Di- <i>cis</i> -propenylmercury ^a	Di- <i>trans</i> -propenylmercury ^a	Divinylmercury ^b
δ_{A} , p.p.m.	...	-6.183	-6.183	-7.297
δ_{B} , p.p.m.	-5.532	-6.932	...	-6.495
δ_{C} , p.p.m.	-4.807	...	-5.592	-5.955
δ_{X} , p.p.m.	-1.999	-1.933	-1.933	...
J_{AB} , c.p.s.	...	11.1	...	13.1
J_{BC} , c.p.s.	4.1	3.5
J_{AC} , c.p.s.	19.2	21.0
J_{AX} , c.p.s.	...	1.3	1.3	...
J_{BX} , c.p.s.	1.4	6.5
J_{CX} , c.p.s.	1.4	...	5.0	...
J_{AY} , c.p.s.	...	134	125	128.5
J_{BY} , c.p.s.	256.5	244	...	295.5
J_{CY} , c.p.s.	127.8	...	140	159.6
J_{XY} , c.p.s.	88.2	12	5.0	...

^a δ values are relative to TMS (internal standard) and were taken at 60 Mc. The negative sign indicates a downfield shift. ^b See ref. 8. These values are not directly comparable to those of the propene derivatives since an external cyclohexane standard was used without making a correction for magnetic susceptibility. The TMS to cyclohexane shift of 1.43 p.p.m. has been added to the data for the sake of comparison.

perturbation of line intensities of the two vinyl protons.

The $\text{Hg}^{199}\text{-H}$ couplings confirm the structural assignments. The average value of the *trans* $J_{\text{Hg}^{199}\text{-H}}$ of 250 c.p.s. is observed in both the iso and *cis* derivatives, while the average value of the *cis* $J_{\text{Hg}^{199}\text{-H}}$ of 133 c.p.s. was observed in both the iso and *trans* derivatives. For divinylmercury,⁸ these parameters, $J_{\text{trans}} = 295.5$, $J_{\text{cis}} = 159.6$, and $J_{\text{gem}} = 128.5$ c.p.s., are slightly larger than the above. It is also noted that the B and C protons for the iso derivative (Fig. 1) can be assigned only on the basis of the mercury-proton coupling constants, since the vinyl proton-methyl proton couplings are of the same magnitude.

Recently interest has arisen in metal exchange reactions of organometallic compounds.¹² The observation of mercury satellites rules out the existence of rapid metal atom exchange. To obtain well resolved mercury satellites, the average lifetimes of the species present must be of the order of 1 sec. or longer.¹³ We

(12) C. R. McCoy and A. L. Allred, *J. Am. Chem. Soc.*, **84**, 912 (1962); R. E. Dessy, F. Kaplan, G. R. Coe, and R. M. Salinger, *ibid.*, **85**, 1191 (1963).

(13) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

observed some variation in line widths of both the parent and satellite peaks from sample to sample which

could be interpreted as arising from mercury exchange. This possibility is being studied further.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA

Infrared Spectra and Structures of Metal Carbonyl Derivatives. III.¹ Acetylene and Olefin Derivatives of Group VI Metal Carbonyls

BY INGO W. STOLZ, GERARD R. DOBSON, AND RAYMOND K. SHELINE

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Several new molybdenum and tungsten π -complexes in which carbonyl groups have been replaced by alkene and alkyne ligands have been synthesized through ultraviolet irradiation. Their infrared spectra in the carbonyl stretching region are reported. The stereochemistry and the nature of bonding in such complexes is briefly discussed.

Introduction

There has been reported recently a considerable amount of work in which group VI metal hexacarbonyls have undergone replacement reactions with various nonaromatic ligands under the influence of ultraviolet radiation or heat. The resulting substitution products include those formed utilizing ligands which function primarily as electron donors^{1,2} and those produced through replacement of carbonyl groups with cyclic olefins which function as chelating groups.³

This paper reports the investigation of some group VI carbonyl complexes $M(\text{CO})_{6-x}(\text{L})_x$ ($M = \text{Mo}, \text{W}$) in which L is an alkene or alkyne which replaces a carbonyl group through formation of a single π -bond. Their spectra in the carbonyl stretching region of the infrared are used as the basis of a discussion of the structures and type of bonding which may be expected in such complexes.

Experimental

The complexes investigated were somewhat unstable and their isolation was made difficult because of a tendency toward reversal of the reaction once irradiation was stopped. Therefore the work was limited primarily to an investigation of the changes observed in the carbonyl stretching region of the infrared as the length of irradiation was varied. Because the complexity of the spectra of solutions which contain derivatives in which more than two carbonyls have been replaced makes interpretation difficult and because many such complexes are insoluble in *n*-hexane, the solvent used in this study, assignments have been limited to those for mono and disubstituted complexes only.

Experimental methods differed only slightly from those used in previous work.^{1b} The solubilities of the π -complexes in nonpolar solvents were, as one might expect, greater than those observed for complexes containing electron-donating ligands. It was therefore feasible to employ *n*-hexane as a common solvent for the photoproduction of the complexes investigated. In addition to being inert to substitution, this solvent permitted the resolu-

tion of close-lying infrared bands. For diethylacetylene, which unlike the other ligands is a liquid at room temperature, 1 ml. was dissolved in 40 ml. of *n*-hexane and the irradiation was carried out under a nitrogen atmosphere.

As a check on the assignments the complexes $\text{W}(\text{CO})_5(\text{propylene})$, $\text{W}(\text{CO})_4(\text{propylene})_2$, $\text{W}(\text{CO})_5(\text{butadiene})$, and $\text{W}(\text{CO})_4(\text{butadiene})_2$ were isolated and purified.

Propylenetungstenpentacarbonyl and Butadienetungstenpentacarbonyl.— $\text{W}(\text{CO})_6$ (200 mg.) was dissolved in 40 ml. of *n*-hexane and pure propylene or butadiene was bubbled through the solution for 15 min. before the irradiation was begun. The solution was then exposed to ultraviolet radiation from a G.E. A-H6 mercury arc lamp for 10 min., during which time propylene or butadiene was continuously bubbled through the solution. The reaction mixture was then frozen and the solvent removed by vacuum distillation. Purification was effected by twice vacuum-subliming the residue from an ice bath. The two complexes were volatile, difficult-to-crystallize solids which decomposed rapidly in air and slightly even under nitrogen. Propylenetungstenpentacarbonyl is whitish in color, while the corresponding butadiene complex is pale yellow.

Anal. Calcd. for propylenetungstenpentacarbonyl: C, 26.25; H, 1.65. Found: C, 25.64; H, 1.47. Calcd. for butadienetungstenpentacarbonyl: C, 28.59; H, 1.60. Found: C, 28.40; H, 1.51.

Di-(propylene)-tungstentetracarbonyl and Di-(butadiene)-tungstentetracarbonyl.—A fresh solution of $\text{W}(\text{CO})_6$ and propylene or butadiene in *n*-hexane (as described above) was irradiated for 150 min., during which time propylene or butadiene was continuously bubbled through the solution. After the irradiation was completed and the solvent removed by vacuum distillation, the impure product was vacuum-sublimed at 35°. The sublimate was then allowed to stand on the cold finger for about 2 hr.; the complex, being more volatile than the $\text{W}(\text{CO})_6$, sublimed on the upper of the cold finger while $\text{W}(\text{CO})_6$ remained on the bottom. The two complexes are pale yellow, oily substances and are quite unstable. This instability made analysis impractical, but solutions of the products in *n*-hexane showed the single sharp carbonyl stretching peak to be expected for *trans*-disubstituted complexes.

Figure 1 illustrates typical spectra observed when a solution of $\text{W}(\text{CO})_6$ and acetylene in *n*-hexane is irradiated for successively longer periods of time. Panel 1 shows the spectrum of the solution before irradiation; the weaker of the two bands is probably the C^{13} analog of the more intense band, the CO stretch for $\text{W}(\text{CO})_6$. After a short period of irradiation (panel 2) three new peaks are observed, corresponding to those predicted for the monosubstituted carbonyl. Panel 3, which illustrates a spectrum taken after further irradiation, shows a decreased $\text{W}(\text{CO})_6$ intensity, an increase in the intensities of the peaks assigned for

(1) The first two papers in this series: (a) G. R. Dobson, M. A. El Sayed, I. W. Stolz, and R. K. Sheline, *Inorg. Chem.*, **1**, 526 (1962); (b) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *ibid.*, **2**, 323 (1963).

(2) H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4455 (1962). This paper lists references to such work.

(3) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).