Y-749. We are grateful to the Chemistry Department of The University of Texas at Dallas for the use of the JEOL JNM-FX200 FT-NMR spectrometer and particularly to Dr. Dean Sherry for his assistance with the FT NMR measurements.

Registry No. 1a, 15218-80-1; **1b**, 80422-34-0; **1c**, 64707-51-3; **2**, 80422-35-1.

Catalytic Polymerization of Acetylenes and Olefins by Tetrakis(acetonitrile)palladium(II) Bis(tetrafluoroborate)

Ayusman Sen* and Ta-Wang Lai

Chandlee Laboratory, Department of Chemistry
Pennsylvania State University
University Park, Pennsylvania 16802

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Summary: The cationic Pd(II) compound $[Pd(CH_3CN)_4](BF_4)_2$ was found to catalyze the polymerization of H—C≡C—R (R = Ph, COOMe), styrene, α-methylstyrene, 1,3-cyclohexadiene, norbornylene, and norbornadiene under very mild conditions. The polyacetylenes are highly colored and have relatively high molecular weights. The poly(phenylacetylene) has a trans configuration around the C=C bond. The polymerization of 1,3-cyclohexadiene leads predominantly to the 1,2 polymer with only minimal cross-linking. The norbornane framework is retained during the polymerization of norbornylene. The poly(norbornadiene) is a highly cross-linked material.

We wish to report that the cationic Pd(II) compound $[Pd(CH_3CN)_4](BF_4)_2$, 1,[1] is a versatile catalyst for the polymerization of a wide range of acetylenes and olefins under relatively mild conditions. Except for a few halides of transition metals in high oxidation states, e.g., $TiCl_4$ and $FeCl_3$, transition-metal compounds in general have not been found to catalyze the cationic polymerization of olefins.[2] This is particularly true for the "softer" transition metals belonging to the second and third period of group 8. However, we have recently presented evidence for the generation of carbonium ions by the interaction of olefins with 1.[3] Therefore, it should be expected that 1 would act as a good initiator for cationic polymerization reactions. Indeed, we find this to be true, and our results are summarized in Table I. These reactions all involved the addition of 100 equiv of the monomer to a 1×10^{-2} M solution of 1 and were carried out under air- and moisture-free conditions by using standard vacuum line techniques. Consistent with a cationic polymerization mechanism, we found that compared to phenylacetylene, the polymerization of the electron-deficient methyl propiolate took place only at a significantly higher temperature and led to a polymer with lower molecular weight. Similarly, no polymerization was observed for the electron-deficient olefins, acrylonitrile and methyl acrylate.

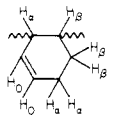
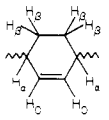
The polyacetylenes are soluble in organic solvents and are highly colored, consistent with the presence of extensive conjugation. The poly(phenylacetylene) shows a maxima at 237 nm (ϵ 1.8×10^6 M^{-1} cm^{-1}, mol wt 9000) with a shoulder at 339 nm (ϵ 6.4×10^5 M^{-1} cm^{-1}) in THF. The corresponding maxima and shoulder for poly(methyl propiolate) are at 232 nm (ϵ 1.85×10^5 M^{-1} cm^{-1}, mol wt 3000) and 291 cm (ϵ 9×10^4 M^{-1} cm^{-1}), respectively. The poly(phenylacetylene) that we have obtained has one of the highest molecular weights recorded thus far.[4] Its infrared spectrum (KBr pellet) exhibits an absorption at 1595 cm^{-1}, indicating the presence of polyconjugated C=C bonds. Two strong bands appear at 755 and 695 cm^{-1}, and these correspond to the C–H out-of-plane deformations of monosubstituted benzene rings. The region between 2000 and 1700 cm^{-1} also exhibits the characteristic absorption of monosubstituted benzenes. In addition, a band at 910 cm^{-1} indicates a trans configuration around C=C bond.[5] When $CHCl_3$, instead of CH_3CN, was used as the solvent, a slightly different polymer exhibiting infrared bands at both 910 and 870 cm^{-1} was obtained. The latter band can be ascribed to a cis configuration around the C=C bonds.[5] Thus the stereostructure of the poly(phenylacetylene) obtained appears to be solvent dependent—in acetonitrile predominantly trans polymer

Table I. Catalytic Polymerization of Olefins and Acetylenes by $[Pd(CH_3CN)_4](BF_4)_2$ [a]

monomer	solvent	temp, °C	time	yield,[b] %	$\bar{M}_n$[c]
H—C≡C—Ph	CH_3CN	25	5 min	30	9000
H—C≡C—CO_2Me	CH_3CN	70	12 h	>90	3000
CH_2=CHPh	CH_3CN	25	5 min	>90	70000
CH_2=C(Me)Ph	CH_3NO_2	0	5 min	75	8000
	CH_3CN	25	30 min	40	2000
	CH_3NO_2	25	5 min	>90	*d*
	CH_3NO_2	25	60 min	>90	*d*

[a] A monomer to catalyst ratio of 100:1 was used in all cases. [b] Yields reported are those of isolated pure materials. [c] Molecular weights of polymers were determined by gel permeation chromatography using solutions of polymers in tetrahydrofuran. A 500-Å microstyragel column was used. The weights reported are those of standard polystyrene samples having GPC traces similar to those observed. [d] The polymer was insoluble in THF.

Table II. Expected ^1H NMR Data for Poly(1,3-cyclohexadiene)

	1,2-polycyclohexadiene	1,4-polycyclohexadiene
		
$H_o/(H_\alpha + H_\beta)$	1/3	1/3
H_α/H_β	1/1	1/2

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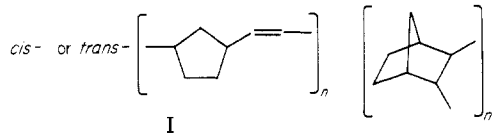
being obtained, while a cis–trans mixture resulted in chloroform. The ^1H NMR spectrum of poly(phenylacetylene) exhibits only a broad featureless absorption between 7.5 and 6.5 ppm.

The ^1H NMR spectrum of poly(1,3-cyclohexadiene) exhibits three broad resonances at 5.8 ppm (H_0), 2.0 ppm (H_α), and 1.6 ppm (H_β), the first two representing respectively the vinylic and allylic protons present in the polymer. Two possible types of polymers (1,2 and 1,4) may arise through the cationic polymerization of 1,3-cyclohexadiene,[6] and these are shown in Table II. The ratio, H_α/H_β, in the polymer that we have obtained is approximately 1, thus indicating it is predominantly 1,2-poly(1,3-cyclohexadiene). The ratio, $H_0/(H_\alpha + H_\beta)$, is a measure of the degree of branching or cross-linking that is present in the polymer ($H_0/(H_\alpha + H_\beta) = 0.33$ for unbranched polymer and 0 for completely cross-linked polymer). In the present case, $H_0/(H_\alpha + H_\beta) = 0.28$, thus indicating the presence of a very modest degree of cross-linking.

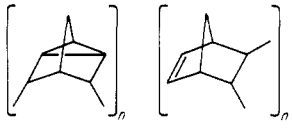
The polymerization of norbornylene has been reported to yield either of the following two polymeric structural units I[7] and II.[8] Structure I, having vinyl cyclopentane



I II

as the repeating unit, is characterized by vinylic resonance at ~5.3 ppm in the ^1H NMR spectrum and C=C stretch at 1680 cm^{-1} and vinylic C-H bending mode at 960 cm^{-1} in the infrared spectrum respectively.[7] On the other hand, the above olefinic features are absent in poly(norbornylene) having II as the structural unit. Instead, the latter type of polymer exhibits an intense absorption at 1300 cm^{-1} in the infrared spectrum, characteristic of the bridging methylene group. The poly(norbornylene) that we have obtained appears to have structure II. It shows none of the spectral features ascribable to the presence of olefinic functionality, while its infrared spectrum (KBr pellet) shows an intense absorption at 1298 cm^{-1} due to the presence of the bridging methylene group.

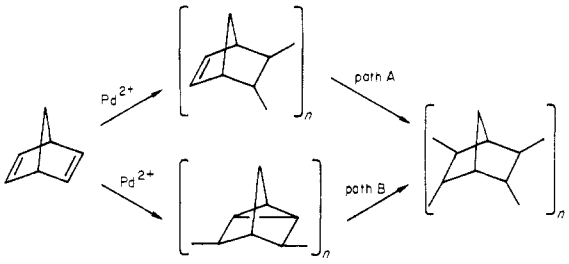
It has been reported that the cationic polymerization of norbornadiene leads to a polymer with the structural unit III.[9] This repeating unit, nortricyclene, is characterized



III IV

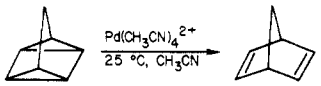
by a strong infrared absorption band at 810–800 cm^{-1}.[10] On the other hand, the polymerization of norbornadiene by π-allyl compounds of Pd(II) results in a polymer with the repeating unit IV.[11] The NMR and IR data presented

Scheme I



appear to support this conclusion.[11] The absence of an infrared absorption at 810–800 cm^{-1} would seem to exclude the presence of the nortricyclene repeating unit. On the other hand, an absorption at 1620 cm^{-1} together with a resonance at 6.2 ppm in the ^1H NMR spectrum indicate the presence of C=C bond. The infrared spectrum of the poly(norbornadiene) that we have obtained show bands at *both* 800 cm^{-1}, which is characteristic of nortricyclene derivatives, and at 1620 cm^{-1}, which indicates the presence of C=C bonds in the polymer. Support for the presence of C=C bonds in our poly(norbornadiene) was also obtained by reacting norbornadiene with 1 in CH_3CN. A soluble polymer with resonance at 6.2 ppm in the ^1H NMR spectrum was obtained. Thus it appears that our poly(norbornadiene) incorporates both repeating units III and IV.

We find our poly(norbornadiene) to be virtually insoluble in all common organic solvents, and this insolubility is probably a consequence of the presence of extensive cross-linking. The cross-linking may arise out of the reaction of the remaining C=C bonds (path A, Scheme I) or through ring-opening polymerization of notricyclene (path B, Scheme I). While our observation of the polymerization of norbornylene by 1 (vide supra) constitutes support for path A, some evidence for path B is provided by the fact that 1 was found to catalyze the instantaneous conversion of quadricyclane to norbornadiene; the latter, if left in the reaction mixture, is then slowly polymerized (eq 1).



(1)

In conclusion, it is obvious that the cationic Pd(II) compound $[Pd(CH_3CN)_4](BF_4)_2$ containing weakly coordinating CH_3CN ligands, is capable of polymerizing a wide variety of acetylenes and olefins. There are also several reports in the literature concerning the catalytic oligomerization and cooligomerization of olefins by Pd(II) compounds which attest to the increased activity of the cationic Pd(II) species as compared to their corresponding neutral precursors.[12] Moreover, the recent report[13] of polymerization of 1,3-butadiene and 1,3-cyclohexadiene by the related cationic Rh compound $[Rh(NO)(CH_3CN)_4](BF_4)_2$ appears to indicate a common reactivity pattern for cationic transition-metal compounds containing weakly coordinating ligands. Indeed, we have observed similar catalytic chemistry for the cationic compounds $[M(NO)_2(CH_3CN)_4](BF_4)_2$ (M = Mo, W).[14] On the other

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hand, the Ni(II) and Co(II) compounds $[M(CH_3CN)_6](BF_4)_2$ (M = Ni, 2; M = Co, 3)[15] were inactive as polymerization catalysts under conditions employed for the reactions involving the Pd(II) compound, 1, even though from a consideration of charge/radius ratios, one might expect Co^{2+} and Ni^{2+} to be more electrophilic than Pd^{2+}.[16] One reason for this remarkable difference in reactivity may be that the CH_3CN ligands in 2 and 3 are held more strongly[17] than those in 1. For example, we find that while the coordinated CH_3CN molecules in 1 exchange "instantaneously" with the solvent when 1 is dissolved in CD_3CN at 25 °C, no exchange was observed in case of 2 even on heating the corresponding solution of 2 to 60 °C for 8 h. Thus, it would appear that the replacement of CH_3CN by olefins or acetylenes in the coordination sphere of the metal is a prerequisite for the polymerization of these substrates.

Finally, from a practical standpoint, an important advantage of using 1 as a catalyst for cationic polymerizations as compared to traditional initiators such as $HBF_4 \cdot Me_2O$ is that the latter does not initiate the polymerization of acetylenes such as phenylacetylene and methyl propiolate under the mild conditions that are employed when 1 is used as the initiator.

Acknowledgment. Financial support of this research by grants from the Department of Energy, Office of Basic Energy Sciences, and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. $(H{-}C{\equiv}C{-}Ph)_n$, 25038-69-1; $(H{-}C{\equiv}C{-}CO_2Me)_n$, 27342-21-8; $(CH_2{=}CHPh)_n$, 9003-53-6; $(CH_2{=}C(Me)Ph)_n$, 25988-53-8; $(1,3\text{-cyclohexadiene})_n$, 27986-50-1; $(\text{norbornene})_n$, 25038-76-0; $(\text{norbornadiene})_n$, 27859-77-4; $[Pd(CH_3CN)_4](BF_4)_2$, 21797-13-7.

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Book Reviews

Reactivity of Metal–Metal Bonds. Edited by M. H. Chisholm. ACS Symposium Series No. 155. American Chemical Society, Washington, D.C. 1981. vii + 327 pages. $39.00.

This 300+ page collection of 15 lectures presented on August 25–26, 1980, at the 180th National ACS Meeting in Las Vegas continues in the tradition of the many excellent ACS Symposium Series in the past. The premise of the symposium on "Reactivity of Metal–Metal Bonds" was that the chemistry of compounds containing metal–metal bonds is shifting from elucidating structures, bonding, and electronic properties to studies concerning reactivity patterns.

About half of the 15 chapters in this book deal with a wide variety of bimetallic systems. Articles by Cotton, Chisholm, McCarley, and Walton discuss group 6 or 7 metal–metal complexes containing triple or quadruple bonds. The first is an historical perspective; the other three present recent results from the authors' labs concerning fundamental reactions of Mo≡Mo complexes, formation of group 6 tetranuclear halo and ternary oxide complexes, and cleavage of metal–metal multiple bonds, respectively. Balch and Puddephatt discuss the preparation and reaction of 1,2-bis[(diphenylphosphino)methane]-bridged Rh, Pd, and Pt complexes containing μ-alkylidene, μ-hydrido, or μ-alkyl ligands, while Curtis presents some recent chemistry of $Cp_2Mo_2(CO)_4$ having to do with addition of reagents across the triple bond. Dyke et al. summarize some fascinating recent chemistry of dimetallacyclic complexes prepared by adding simple molecules (e.g., acetylenes) to metal–metal bonded dimeric complexes. A related paper by Ashworth et al. describes some simple preparative routes to complexes containing two (or three) metals, many of them based on the principle of "oxidizing" Pt(0) by adding a M=C or M≡C bond to it.

Metal cluster chemistry is represented here in two chapters, one by Vidal on polynuclear rhodium carbonyl complexes and a second by Geoffroy on $H_2FeRu_3(CO)_{13}$.

The remaining four chapters are relatively thorough, general accounts of the photochemistry of metal–metal bonds (Wrighton), the kinetics of reactions involving metal carbonyl dimers and trimers (Pöe), the thermochemistry of metal–metal bonds (Connor), and the coordination chemistry of metal surfaces (Muetterties).

Like previous books in this series, this one is assembled from camera-ready manuscripts. While technical quality is sacrificed to some extent for speed of publication, the authors have for the most part made the book more readable by using the same typeface and format. An index is included.

Richard R. Schrock, *Massachusetts Institute of Technology*

Catalytic Activation of Carbon Monoxide. Edited by P. C. Ford. ACS Symposium Series No. 152, American Chemical Society, Washington, D.C. 1981. ix + 358 pages. $36.50.

This volume is a collection of 21 papers presented at a symposium at the American Chemical Society Meeting in Las Vegas in 1980 and is part of the ACS Symposium Series. The field of CO activation is continually gaining importance as the search goes on for replacements for petroleum feedstocks, and this volume presents a good overview of research in this field in the past few years. The majority of the papers deal in some way with homogeneous catalysis of CO activation, either by describing the synthesis and reaction chemistry of compounds which are models for proposed reaction intermediates or by describing actual catalyst systems. There are six papers by various research groups describing different systems for the homogeneous catalysis of the water gas shift reaction. In total, these papers cover nearly all of the most recent work in this field. Of particular note here is a very detailed paper by Slegeir, Sapienza, and Easterling on "Mechanistic Aspects of the Homogeneous Water Gas Shift Reaction". The paper by Dombek on the "Hydrogenation of Carbon Monoxide to Methanol and Ethylene Glycol by Homogeneous Ruthenium Catalysts" and that by Feder, Rathke, Chen, and Curtiss on "Experimental and Theoretical Studies of Mechanisms in the Homogeneous Catalytic Activation of Carbon Monoxide" are good examples of research on the direct production of C_1 and C_2 oxygenated chemicals by CO hydrogenation. The paper by Knifton on "Syngas Homologation of Aliphatic Carboxylic Acids" provides an interesting example of the incorporation of CO into other molecules.

There are seven papers which discuss the synthesis and reaction chemistry of organometallic compounds believed to be models for reactive intermediates in CO hydrogenation. A particularly intriguing paper in this area is the contribution by Gladysz, Kiel, Lim, Wary, and Tam, which discusses the reaction chemistry of