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Synthesis and Characterization of a New Class of Organo-polynuclear Complexes Containing Cationic Palladium Atoms

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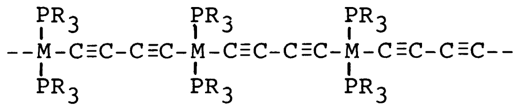
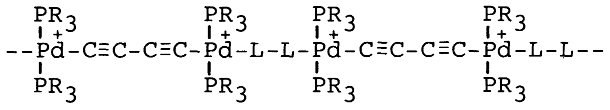
Cationic organopalladium complexes having an extended structure are described as a new class of organo-polynuclear complexes containing ionic transition metals with regular arrangement in the main chain.

Organometallic polymers have drawn much attention in terms of their unique physical properties and catalyses.1) However, there are few examples of organometallic polymers containing transition metals in the main chain.2,3) We previously synthesized transition metal-poly(yne) polymers (**1**) which have a backbone composed of transition metals and conjugated acetylenic linkages.3) Here we wish to report the synthesis and properties of a new type of polynuclear complexes (**2**) which have unique backbones composed of cationic palladium atoms with regular arrangement and alternate linkages of acetylene and bipyridyl.



$$--\overset{PR_3}{\underset{PR_3}{M}}-C\equiv C-C\equiv C-\overset{PR_3}{\underset{PR_3}{M}}-C\equiv C-C\equiv C-\overset{PR_3}{\underset{PR_3}{M}}-C\equiv C-C\equiv C--$$

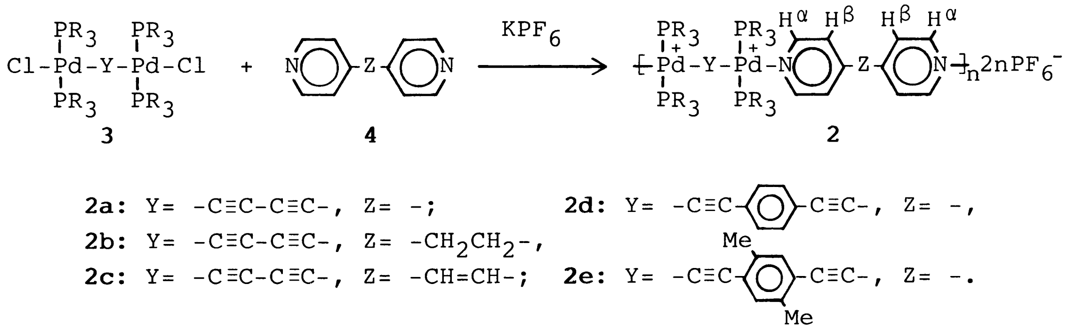
1



$$--\overset{PR_3}{\underset{PR_3}{Pd^+}}-C\equiv C-C\equiv C-\overset{PR_3}{\underset{PR_3}{Pd^+}}-L-L-\overset{PR_3}{\underset{PR_3}{Pd^+}}-C\equiv C-C\equiv C-\overset{PR_3}{\underset{PR_3}{Pd^+}}-L-L--$$

2

Thus, μ-butadiynediyl-bis[trans-chlorobis(tri-n-butylphosphine)-palladium](**3a**)4) was reacted with 4,4'-bipyridyl (molar ratio, 1/1) in the presence of excess KPF_6 in acetone to give an ionic organo-polynuclear complex (**2a**, $Y= -C\equiv C-C\equiv C-$, Z= -, R=n-Bu) in 88% yield as yellow solids; decomp. at 104-108 °C, $[\eta]=0.97$ dL/g in dichloromethane at 25 °C. The average molcular weight of **2a** was tentatively obtained to be ca. 10000 by VPO and NMR methods (vide infra), which corresponds to n=ca. 6, and hence **2a** has about twelve palladium atoms in a molecule. The polynuclear complex is stable in air and soluble in polar organic solvents such as dichloromethane and acetone. The structure was characterized by spectral methods. The $^{31}P\{^1H\}$ NMR spectrum showed a single peak due to the PBu_3 ligands at 16.25 ppm down field from an external PPh_3 reference, and the resonance due to the PF_6 appeared at 138.84 ppm up field from the reference ($J_{P-F}=711$ Hz), indicating that the terminal groups of **2a** are not chlorine atoms but bipyridyl ligands. The ^1H-NMR (360 MHz) exhibited resonances of H^α at δ 9.06 and H^β at 8.27 along with weak resonances at δ 8.79 and 7.82. The latter pair may be assigned to the hydrogens bonded to uncoordinated pyridyl moieties of the terminal bipyridyl ligands and used for molecular weight estimation. These spectral data are



consistent with a regular structure of **2a**. As compared with the neutral polymers (**1**), the stretching frequencies of C≡C in the IR specta of **2** shift to higher frequencies and the phosphorus chemical shifts in ^{31}P-NMR spectra to lower magnetic fields due to the cationic character of the palladium atoms. Polynuclear complex **2a** showed electric conductivities in polar solvents; 596 $\mu\Omega^{-1}$cm^{-1} in acetone, 754 in nitromethane.

Similarly several analogues (**2b-e**) were prepared from the reaction between selected pairs of the dihalides (**3**) and bipyridyl derivatives (**4**). They may provide a new class of ionic organo-polynuclear complexes having transition metals in the main chain, though some metallocene polymers containing ferricinium$^{5)}$ and cobalticinium$^{6)}$ species are known. The concentrated solutions of the polynuclear complexes such as **2a** and **2d** in dichloromethane exhibited formation of nematic liquid crystals indicating that the polynuclear complexes have an extended linear structure.$^{7)}$ The high resolution ^{31}P{^{1}H} NMR study$^{7)}$ of the lyotropic liquid crystals revealed that poylnuclear complex **2a** aligned its main chain in the direction parallel to the applied magnetic field (23.5 kG; 1 G=10^{-4} T).$^{8)}$

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References

1) See, for example, W. T. Ford, CHEMTECH, 1987, 246.
2) E. C. Carraher, Jr., J. E. Sheats, and C. U. Pittman, Jr., "Organometallic Polymers," Academic Press, New York (1978).
3) N. Hagihara, K. Sonogashira, and S. Takahashi, Adv. Polym. Sci., 41, 149 (1980).
4) S. Takahashi, Y. Ohyama, E. Murata, K. Sonogashira, and N. Hagihara, J. Polym. Sci., Polym. Chem. Ed., 18, 349 (1980).
5) T. Ito and T. Kenjo, Bull. Soc. Chem. Jpn., 41, 614 (1968); C. U. Pittman, Jr., J. C. Lai, D. P. Vanderpool, M. Good, and R. Prado, Macromolecules, 3, 746 (1970).
6) C. U. Pittman, Jr., O. E. Ayers, S. P. McManus, J. E. Sheats, and C. E. Whitten, Macromolecules, 4, 360 (1971).
7) S. Takahashi, E. Murata, M. Kariya, K. Sonogashira, and N. Hagihara, Macromolecules, 12, 1016 (1979).
8) S. Takahashi, Y. Takai, H. Morimoto, and K. Sonogashira, J. Chem. Soc., Chem. Commun., 1984, 3.

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