6250 Journal of the American Chemical Society / 101:21 / October 10, 1979

Bimetal Vapor–Polymer Chemistry at Close to Room Temperature. A New Synthetic Pathway to Mononuclear and Cluster Bimetallic Polymers

Colin G. Francis, Helmut Huber, and Geoffrey A. Ozin*

Contribution from the Lash Miller Chemistry Department and Erindale College, University of Toronto, Toronto, Ontario, Canada. *Received March 26, 1979*

Abstract: The simultaneous or sequential codeposition of two different metal vapors into a liquid film of a poly(methylphenylsiloxane) has been designed to yield organometallic polymers containing both mononuclear and cluster metal sites. These bimetallic polymers are formed at close to room temperature and are amenable to characterization by a number of different types of spectroscopy.

Introduction

The majority of bimetallic cluster catalysts in operating systems today are of the highly dispersed supported heterogeneous variety and, by their very nature, are usually poorly defined and therefore difficult to understand at an atomic level,[1] although electron microscopy,[2] Mössbauer,[3] and EXAFS[4] methods are clarifying some critical structural and electronic features at the active metal sites.

In this paper, we consider a possible useful approach to the design of a new kind of bimetallic cluster system of a well-defined type, comprising a few metal atoms at the active sites. Based on a number of experimental and theoretical results concerning very small metal clusters, such a nuclearity regime is anticipated to display rather unique catalytic behavior.[5]

Liquid polymers with suitable functional groups, capable of acting as solvating or complexing sites, offer an attractive medium in which to generate and immobilize low nuclearity, unimetallic, and bimetallic clusters under homogeneous reaction conditions. We have discovered that a combination of metal vapor–liquid polymer synthetic techniques can be successfully employed to control the competing processes of metal atom diffusion, aggregation, and anchoring, significantly, at close to room temperature. The method permits a unique route into the generation of polymer-stabilized, unimetallic few-atom clusters.[6]

The method can be extended to encompass a range of bimetallic combinations, the Ti/Cr system being used in this paper to illustrate the approach to polymer-supported bimetallic species. One might envisage such unimetallic or bimetallic polymers being incorporated into, for example, a fluid bed reactor for catalyzing a variety of chemical processes.

Experimental Section

The technique is basically an extension of the oil matrix method developed by Blyholder[7] to produce large metal particles suspended in an inert paraffin oil. Such suspensions were subsequently used to investigate the chemisorption of small molecules on the metal particle surfaces by various forms of spectroscopy.

In our method, a thin film ($\sim 10^{-6}$ m) of a polymeric fluid, containing reactive functional groups, is applied to a quartz optical plate cooled to 0 to −30 °C by means of an Air Products Displex refrigeration system. An evaporation source, equipped with quartz crystal microbalance for continuous measurement of the metal deposition rate, is used to deposit metal vapor into the liquid film, typically at a rate of approximately 0.2 μmol h^{-1}.

By means of ultraviolet–visible spectroscopy, the formation of products under various experimental conditions, such as metal deposition rate, metal loading, functional group loading, and reaction temperature, may be quantitatively monitored.

Results and Discussion

In an earlier report,[8] one of us (C.G.F.) demonstrated that Ti, V, Cr, and Mo vapors can be deposited into a liquid poly(methylphenylsiloxane), Dow Corning 510, containing a Me:Ph ratio of 17:1. The reactions were carried out in a rotary reactor in the temperature range 0 to −20 °C to yield liquid organometallic polymers in which two phenyl groups were coordinated to the metal to give an anchored bis(arene) complex.

In a rotary reactor,[9] the thin film of the polymeric liquid which interacts with the metal vapor is continually being replenished at both a macroscopic level, as a result of mixing with the reservoir in the bottom of the flask, and at a microscopic level, owing to the mobility of the polymer chains. It is likely that the motion of the chains on a microscopic scale is very fast compared with the bulk motion of the fluid and, with this proposal in mind, we considered that a thin film of fluid adhering to an optical window might provide a useful spectroscopic probe of the microscopic details of metal vapor–liquid polymer interactions. In this way one would hope to be able to identify reaction intermediates, as well as products, with the idea of relating the spectroscopic observations to those emerging from the macroscale synthesis.

Our initial observations with the metal vapor–fluid matrix reactions focused on the quantitative aspects of chromium vapor–DC510 interactions. These experiments involved monitoring the decay of one of the absorbances due to free phenyl groups (214 nm) and the corresponding growth of the absorbances due to products, a typical reaction sequence being illustrated in Figure 1(I). The evolution of the various products can be depicted in graphical form, Figure 1(II), an analysis of which indicates a reaction sequence of the type shown in Scheme I.

Support for the existence of such cluster species is provided by the mass spectroscopic observation of ion-molecular reactions in the (π-C_6H_6)Cr(CO)$_3$ system,[10] leading to the formation of $(C_6H_6)_2Cr_2^+$ and $(C_6H_6)_2Cr_3(CO)_n^+$. It has also been shown recently that chromium vapor deposited into a C_6H_6/Ar matrix at 10–12 K shows an optical spectrum indicating the presence of a number of arene–metal species.[11] Metal concentration studies have established that these species are binuclear in chromium.

One can envisage the creation of polymer-stabilized few-atom clusters in this system as arising from phenyl group solvation effects or bis(arene) metal cluster complexation. The early impression is one of a gradually diminishing metal–arene interaction as the cluster nuclearity increases until, at values of n greater than 3, metal cluster desolvation occurs to release clusters containing of the order of four to six atoms possessing bulk-like optical absorptions,[12] namely, broad resonances in the region 200–300 nm for the chromium system (as shown by optical studies using DC200, a polymethylsiloxane).

The discovery of polymer-stabilized few-atom metal clusters

0002-7863/79/1501-6250$01.00/0

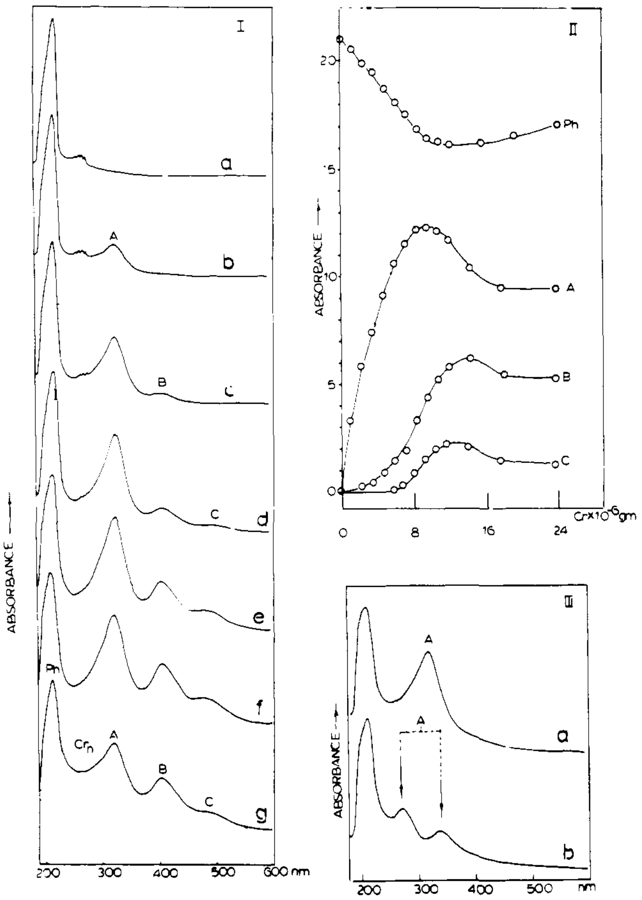


Figure 1. (I) Ultraviolet-visible absorption spectra for the deposition of Cr vapor into DC510 at −20 °C. (II) Graphical representation of the growth and decay of species labeled A, B, C, and Ph in (I). (III) Brief exposure of species A to 1 Torr of oxygen giving conversion to species A'.

in the chromium and other systems prompted us to attempt to prepare systems containing two different metals. In this report we focus our attention on the Ti/Cr vapor-DC510 system.

A quantitative titanium vapor-DC510 titration curve is illustrated in Figure 2 and shows the decrease and leveling off of the absorbance due to uncoordinated phenyl groups as titanium vapor is deposited into the fluid. This is accompanied by growth of at least two distinct titanium-containing species, absorbing at 355 nm (species A) and a broad band around 560-610 nm (species B).

The growth behavior and band-shape variation of this latter absorption as a function of titanium concentration could indicate the presence of more than a single species. By comparison with the optical spectra of bis(benzene) metal complexes[14] the intense ultraviolet band at 355 nm and a very weak visible band around 504 nm are assigned respectively to the metal to ligand charge transfer and ligand field excitations of polymer-bound bis(arene)titanium. The other titanium-containing species, absorbing in the 560-610-nm region, is assigned to small titanium clusters stabilized by the polymer (*n* probably equal to 2).

Comparison of the optical trends for the postulated polymer-supported small metal cluster species with the data for the known metal clusters[13] in solid argon matrices (Table I) indicates that slightly perturbed metal-localized electronic excitations are primarily responsible for the new visible absorptions in the Cr-, Ti-, and V-DC510 systems.

Having established the optical characteristics of the individual Ti and Cr vapor reactions with DC510 one can investigate the bimetallic system by means of the following reac-

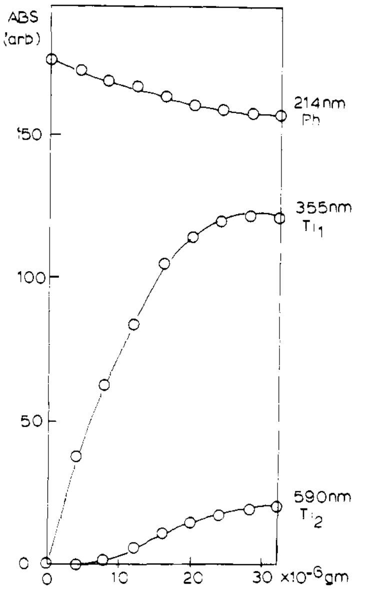
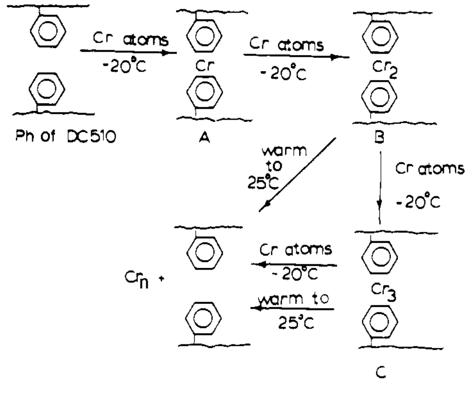


Figure 2. Ultraviolet-visible absorption spectrum for the deposition of Ti vapor into DC510 at −20 °C.

Table I. Visible Absorption Spectra of Small Immobilized Metal Clusters

	argon[13] (10-12 K)	DC510 (0 to −30 °C)
Ti_2	430	
	546	560-590
	624	
Cr_2	460	402
Cr_3	477	479
V_2	494	455
	587	

Scheme I



tions: (1) sequential Ti and Cr vapor deposition, (2) simultaneous Ti/Cr vapor deposition, (3) saturation of the phenyl groups on DC510 with Ti vapor followed by reaction with Cr atoms, (4) saturation with Cr vapor followed by reaction with Ti atoms.

As a small amount of Ti vapor is deposited into the fluid (M:L < 1:50), one observes the expected 355-nm band of polymer-supported bis(arene)titanium (Figure 3). Depositing a small amount of Cr vapor, one observes growth of the 318-nm absorption of the bis(arene)chromium, but also a depletion of the bis(arene)titanium and growth of a new species, labeled CrTi in Figures 3 and 4, absorbing at 442 nm. Support for the assignment is provided by the observation that the new species

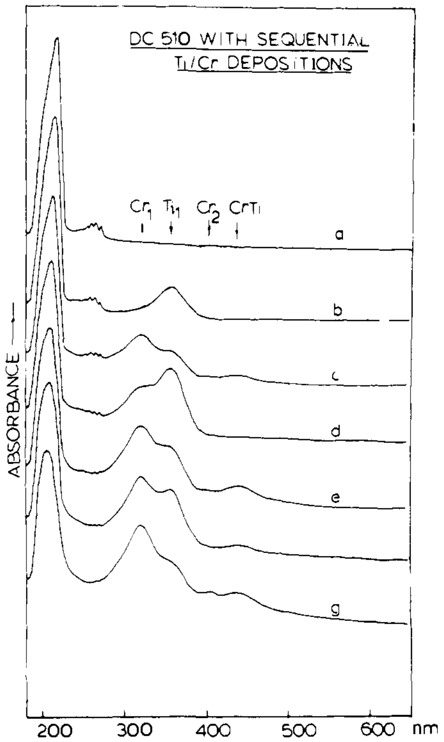


Figure 3. (1) The ultraviolet-visible spectra of sequential quantitative Ti vapor, Cr vapor depositions into DC510 at −20 °C beginning (a) with a thin film of pure DC510 followed by addition of (b) Ti, (c) Cr, (d) Ti, (e) Cr, (f) Ti, and (g) Cr. The polymer-anchored sites are depicted by $Cr_1 \equiv -(C_6H_5)_2Cr$; $Ti_1 \equiv -(C_6H_5)_2Ti$; $Cr_2 \equiv -(C_6H_5)_2Cr_2$; $Ti_2 \equiv -(C_6H_5)_2Ti_2$; $TiCr \equiv -(C_6H_5)_2TiCr$.

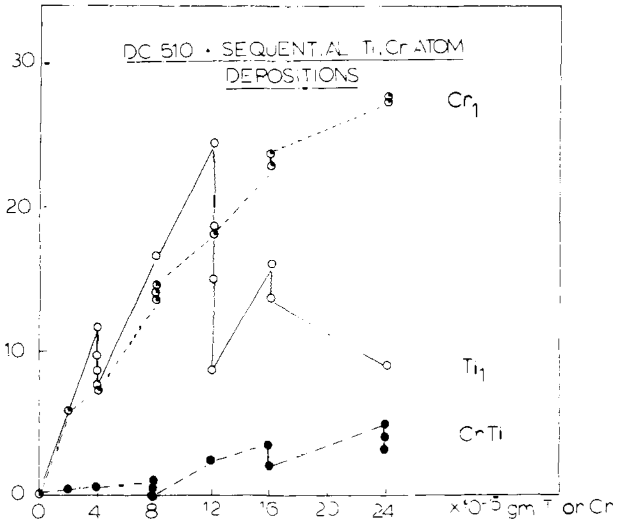


Figure 4. Growth-decay graphical representation of a sequential Ti vapor-Cr vapor deposition of the type shown in Figure 3.

absorbs in a region between the proposed polymer-attached dichromium (402 nm) and dititanium (560-610 nm) cluster species. This is in keeping with the average environment effect for metal-localized excitations of similar origin observed in heterobinuclear cluster carbonyl complexes as well as CrMo in argon.[15]

On depositing more Ti vapor into the film (Figure 3, spectrum d) the polymer-supported bis(arene)titanium grows back in but, while the bis(arene)chromium band does not change, that due to the CrTi species decays appreciably. The growth-decay behavior can be reproduced with further sequential metal deposition up to the phenyl saturation level (Figure 4) at which point some of the dichromium species begins to be formed (Figure 3, spectra e-g).

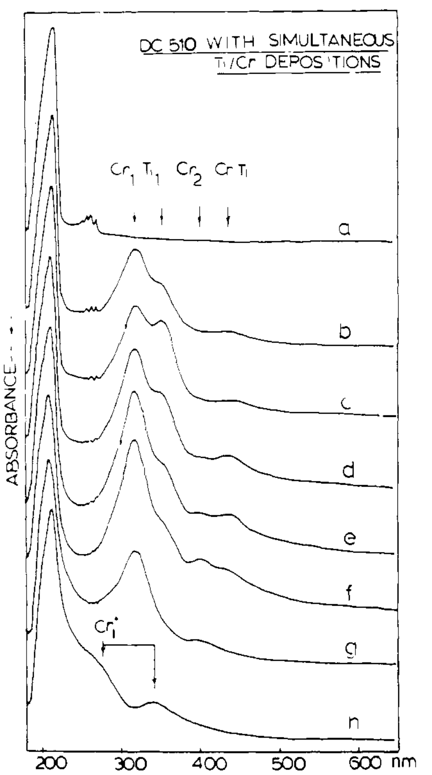
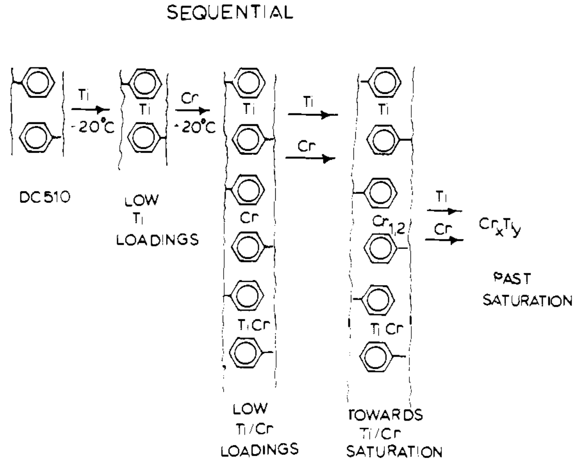


Figure 5. (a-f) Simultaneous Ti vapor-Cr vapor deposition into DC510 at −20 °C. (g) The preferential air oxidation of the Ti anchored species followed by (h) showing the eventual oxidation of the Cr anchored species to the $-(C_6H_5)_2Cr^+$ supported cation.

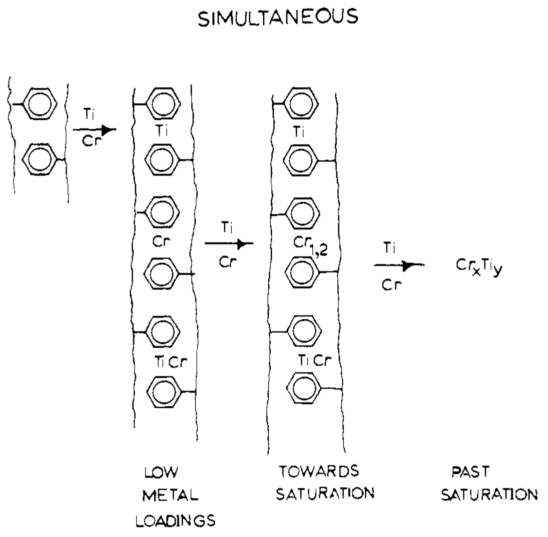
Scheme II



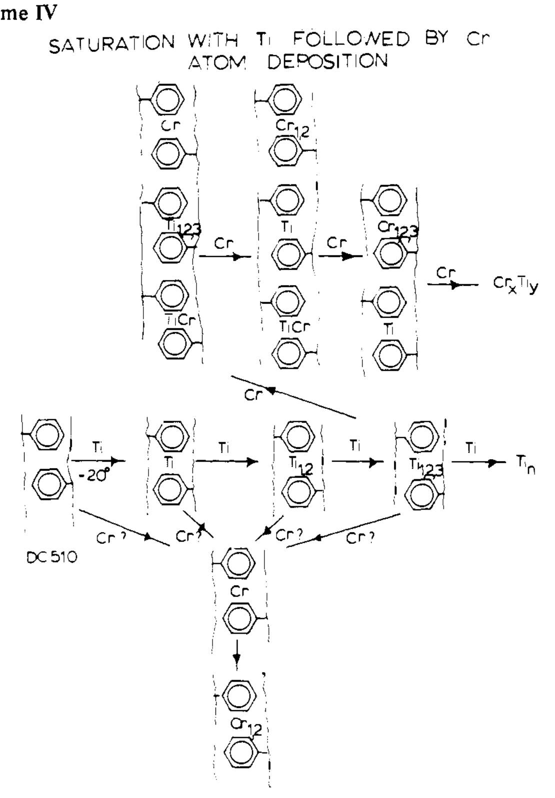
An important difference observed in the simultaneous Ti/Cr deposition is the concurrent appearance of all three species, as the concentration of metal in the fluid is increased (Figure 5, spectrum b). As the concentration increases further, one observes the growth of bis(arene)chromium but the decay of bis(arene)titanium and the CrTi species with eventual growth of the dichromium species (Figure 5, spectra c-f).

A number of aspects of the sequential-simultaneous Ti/Cr depositions into DC510 are clarified by the metal atom saturation experiments. The gradual deposition of Ti atoms into DC510, up to the saturation loading, leads to both polymer-supported bis(arene)titanium and polymer-stabilized two- or three-atom titanium clusters (Figure 6(1), spectrum b). On depositing Cr vapor into this Ti-saturated DC510 fluid one

Scheme III



Scheme IV



observes the decrease of bis(arene)titanium and the cluster species with growth of bis(arene)chromium and the CrTi species (Figure 6(I), spectra c and d). When more Cr vapor is deposited into the fluid, the bis(arene)chromium species increases while the CrTi species increases and then decays. This is accompanied by depletion of the titanium cluster species but eventual formation of the polymer-stabilized dichromium species (Figure 6(I), spectra d-g). These growth-decay curves are depicted as a function of metal loading in Figure 6(II). An important result is the continued consumption of polymer-supported phenyl groups beyond the titanium saturation loading during the deposition of chromium atoms.

In the analogous chromium saturation experiment, on subsequently depositing Ti atoms there is no change in the bis(arene)chromium absorbance, although depletion of the cluster species occurs and one observes *zero* growth of bis(arene)titanium.

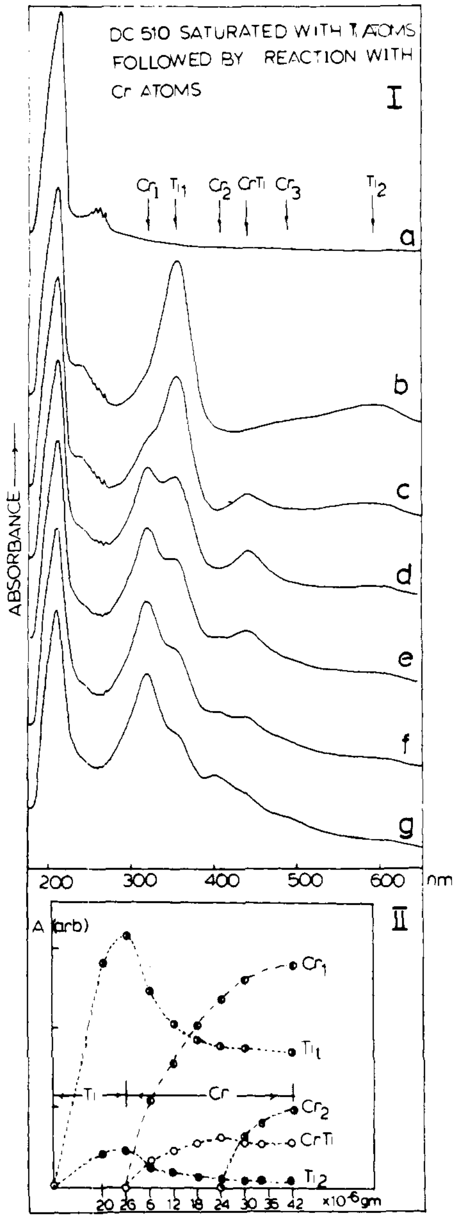


Figure 6. (I) Ultraviolet-visible absorption spectra for a Ti atom saturation experiment into a thin static film of DC510 at −20 °C followed by reaction with Cr atoms. (II) A graphical representation of the growth and decay of the different polymer-anchored metal sites depicted in (I).

A possible explanation of the way in which the metal vapors interact with the DC510 under the different conditions is shown in Schemes II-IV, bearing in mind that bis(benzene)titanium is less thermally stable than bis(benzene)chromium.

Summarizing, it seems likely that our bimetal Ti/Cr depositions with DC510 at low metal loadings are leading to polymer-supported bis(arene) metal complexes with two different mononuclear metal sites attached to the same polymer. At high metal loadings, binuclear sites containing polymer-stabilized Ti_2 and Cr_2 as well as TiCr clusters are formed.

The results of this series of experiments indicate that the titanium-containing species are kinetically unstable toward reaction with Cr atoms; for example, the bis(arene)titanium complex appears to yield the TiCr cluster species. Very high Ti/Cr loadings probably lead to "naked" (unsolvated) Cr_xTi_y bimetallic clusters approaching colloidal dimensions. Unanswered questions relate to the possible concerted displacement of Ti from bis(arene)titanium by Cr atoms to yield the corresponding Cr complex; a similar question applies to the polymer-stabilized titanium cluster elimination by Cr atoms. Further experiments are being attempted to try to establish these details of the Ti/Cr-DC510 reaction.

Acknowledgments. The financial assistance of the National Research Council of Canada's New Ideas, Strategic Energy and Operating Grants programs, Imperial Oil of Canada, the Connaught Foundation, Erindale College, and the Lash Miller Chemical Laboratories is gratefully appreciated.

References and Notes

(1) (a) J. H. Sinfelt and J. A. Cusamano in "Advanced Materials in Catalysis", J. J. Burton and R. L. Garten, Eds., Academic Press, New York, 1977; (b) J. J. Burton and R. L. Garten in ref 1a; (c) J. H. Sinfelt, *Acc. Chem. Res.*, **10,** 15 (1977), and references cited therein.

(2) E. B. Prestridge, G. H. Via, and J. H. Sinfelt, *J. Catal.*, **50**, 115 (1977).

(3) C. H. Bartholomew and M. Boudart, *J. Catal.*, **29**, 278 (1973); R. L. Garten and D. F. Ollis, *ibid.*, **35**, 232 (1974); R. L. Garten, *ibid.*, **43,** 18 (1976); M. A. Vannice and R. L. Garten, *J. Mol. Catal.*, **1,** 201 (1975–1976).

(4) F. W. Lytle, "The Electron Factor in Catalysis on Metals", *Natl. Bur. Stand. (U.S.)*, *Spec. Publ.*, **No. 475,** 34 (1977); F. W. Lytle, D. E. Sayers, and E. B. Moore, Jr., *Appl. Phys. Lett.*, **24,** 45 (1974); I. W. Bassi, F. W. Lytle, and G. Parravano, *J. Catal.*, **42**, 139 (1976); B. Moraweck, G. Clugnet, and A. J. Renouprez, *Surf. Sci.*, **81,** L631 (1979), and references cited therein.

(5) G. A. Ozin, *Catal. Rev. Sci. Eng.*, **16,** 191 (1977); R. P. Messmer in "The Nature of the Surface Chemical Bond", G. Ertl and T. N. Rhodin, Eds., North-Holland Press Publishing Co., Amsterdam, 1979; R. Ugo, *Catal. Rev. Sci. Eng.*, **11,** 225 (1975); E. L. Muetterties, *Science*, **196,** 839 (1977); E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, **79**, 91 (1979); Y. Takasu and A. M. Bradshaw, *Surf. Defect Prop. Solids*, 401 (1978); "The Electron Factor in Catalysis on Metals", *Natl. Bur. Stand. (U.S.)*, *Spec. Publ.*, **No. 475** (1977), and references cited therein.

(6) G. A. Ozin and C. G. Francis, Proceedings of the EUCHMOS Conference on Molecular Spectroscopy, Frankfurt, 1979.

(7) R. Sheets and G. Blyholder, *Appl. Spectrosc.*, **30,** 602 (1976), and references cited therein.

(8) C. G. Francis and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 466 (1977).

(9) R. E. Mackenzie and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 650 (1974).

(10) J. R. Gilbert, W. P. Leach, and J. R. Miller, *J. Organomet. Chem.*, **56,** 295 (1973).

(11) L. Nazar and G. A. Ozin, to be published.

(12) N. Rösch and D. Menzel, *Chem. Phys.*, **13,** 243 (1976); G. Seifert, E. Mrosan, and H. Müller, *Phys. Status Solidi B*, **89**, 553 (1978), and references cited therein.

(13) W. Klotzbücher, R. Busby, and G. A. Ozin, *J. Am. Chem. Soc.*, **98,** 4013 (1976); H. Huber, T. A. Ford, W. Klotzbücher, M. Moskovits, E. P. Kündig, and G. A. Ozin, *J. Chem. Phys.*, **66,** 524 (1977); W. Klotzbücher and G. A. Ozin, *J. Mol. Catal.*, **3,** 195 (1977–1978); *J. Am. Chem. Soc.*, **100**, 2262 (1978).

(14) R. D. Feltham, *J. Inorg. Nucl. Chem.*, **16,** 197 (1961).

(15) H. B. Abrahamson, C. C. Frazier, D. S. Ginley, H. B. Gray, J. Lillienthal, D. R. Tyler, and M. S. Wrighton, *Inorg. Chem.*, **16,** 1554 (1977). W. Klotzbücher, G. A. Ozin, J. G. Norman, Jr., and H. J. Kolari, *Inorg. Chem.*, **16,** 2871 (1977).

Resolutions Using Metal Complexes. Synthesis, Separation into Diastereoisomers, and Resolution of *o*-Phenylenebis(methylphenylphosphine) Using Palladium Complexes Containing Optically Active Ortho-Metalated Dimethyl(α-methylbenzyl)amines

Nicholas K. Roberts and Stanley Bruce Wild*

Contribution from the Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009.

Received April 16, 1979

Abstract: The new chelating di(tertiary phosphine) *o*-phenylenebis(methylphenylphosphine) has been prepared in 68% yield from *o*-dichlorobenzene by reaction with sodium methylphenylphosphide in tetrahydrofuran solution. The racemic and meso forms of the ligand, (*RR;SS*)-diphos and (*RS*)-diphos, respectively, were separated by a combination of direct fractional crystallization of the mixture of diastereoisomers, and by selective precipitation of the sparingly soluble complex $[Ni(SCN)((RS)\text{-diphos})_2]SCN$. The diastereoisomeric di(tertiary phosphines) were subsequently identified by analyzing the ^1H NMR spectra of their respective substituted 1*H*-1,3-benzodiphospholenium salts. Optimized conditions are described for the large-scale resolution of (*RR;SS*)-diphos by a method which involves the separation of internally diastereoisomeric palladium complexes containing the dissymmetric di(tertiary phosphine) and an optically active ortho-metalated dimethyl(α-methylbenzyl)amine. The optically pure enantiomers, $[\alpha]_D \pm 81.5°$ (CH_2Cl_2), are air-stable, crystalline solids, mp 112–113 °C, whose absolute configurations have been determined by X-ray analysis. The optically active di(tertiary phosphines) epimerize rapidly upon heating, although they can be recovered unchanged from concentrated hydrochloric acid solution. Indeed, optically active monoprotonated phosphonium salts can be isolated from these solutions.

Despite the keen interest in the use of soluble rhodium(I) complexes containing optically active di(tertiary phosphines) as catalysts for the asymmetric hydrogenation of prochiral substrate molecules, notably α-amino acid precursors,[1] there is no general and convenient method available, to date, for the resolution of dissymmetric di(tertiary phosphines) containing asymmetric donor atoms. The classical method of fractionally crystallizing diastereoisomeric salts containing an appropriate quaternary derivative of the di(tertiary compound) is fraught with difficulties, among which is the problem of stereospecifically liberating the optically active ditertiary species from the resolved salt. Nevertheless, quaternary *benzyl* salts of bis(methylphenylphosphino)-1,2-ethane[2] and its arsenic analogue[3] have been resolved by this method using D(−)-dibenzoyl hydrogen tartrate as resolving agent and the former has been subsequently reduced by polarographic means to the optically active di(tertiary phosphine), albeit of uncertain optical purity. Another procedure, which obviates the need to resolve a *di*tertiary species, involves the oxidative coupling of α carbanions derived from optically active methyl-substituted mono(tertiary phosphine) oxides. Thus, (+)-(*R*)-ethylmethylphenylphosphine oxide[4] and (+)-*o*-anisylmethylphenylphosphine oxide[5] were dimerized to their respective di(tertiary phosphine) oxides and the latter was subsequently reduced by

0002-7863/79/1501-6254$01.00/0