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Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,5,8-trien-4-yl) Derivatives of the Group IV Transition Metals

Vinayak V. Bhide, Peter L. Rinaldi, and Michael F. Farona*

Department of Chemistry, The University of Akron, Akron, Ohio 44325-3601

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Metallocene dichloride derivatives of titanium, zirconium, and hafnium were prepared from tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene and the corresponding metal tetrachlorides. These compounds were characterized as existing primarily in the endo,endo and exo,endo forms by two-dimensional ^{1}H NMR studies. These results were unexpected, in that theory predicts primarily exo,exo isomers should be preferred. A study on bis(isodicyclopentadienyl)titanium dichloride revealed the compound to exist in two major isomeric forms: exo,endo and exo,exo.

Introduction

Recent reports by Paquette and co-workers on the chemistry of isodicyclopentadiene (diene) and tricyclo[5.2.1.0^{2,6}]-deca-2,5,8-triene (triene) have focused on the structure of the ferrocene and group IV metallocene derivatives of these ligands.[1-3] According to INDO calculations,[4] the high-lying norbornyl σ orbitals in isodicyclopentadiene are strongly coupled to π orbitals in the cyclopentadienide portion of the molecule, resulting in disrotatory tilting of the peripheral lobes toward the methano bridge. Consequently, complexation by small metals, or those in a high oxidation state, should be favored on the exo face, whereas larger metal atoms might prefer coordination to the endo face.[1]

Our interest is in the triene ligand, since metallocenes can be synthesized containing an olefinic group for subsequent reactions. When we synthesized the ferrocene derivative of the triene using reaction times much shorter than those of Paquette and co-workers,[1] the product obtained consisted of all three possible isomers, although the exo,exo isomer was favored.[5] Similar results were found in the product obtained from the diene.[5] This contrasts somewhat with the theoretical predictions and findings of Paquette et al., who obtained exclusively the exo,exo isomer in both cases.[1]

We have now undertaken the synthesis of the triene derivatives of the group IV metallocene dichlorides, which is the subject of this work.

Experimental Section

Starting Materials and Solvents. Benzene (reagent) and tetrahydrofuran were purchased from Fisher and distilled from sodium/benzophenone under nitrogen before used. *n*-Butyllithium was obtained from Alfa Products as a 22%, 2.4 M solution in hexane and used as received. The titanium, zirconium, and hafnium tetrachlorides were purchased from Aldrich and used without further purification.

Tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene[6] and isodicyclopentadiene[7] were synthesized according to literature methods and characterized by melting points, elemental analyses, and NMR spectrometry.

Physical Methods. Proton NMR spectra were recorded on a Varian VXR 300-MHz spectrometer. Two-dimensional NMR spectrometry in the form of homonuclear correlation spectroscopy (COSY)[8] and nuclear Overhauser effect spectroscopy (NOESY)[9] was carried out to elucidate the isomeric forms of the compounds prepared in this research.

All two-dimensional COSY and NOESY NMR spectra were obtained with phase-sensitive detection according to the method of States et al.[10] Two-dimensional NMR symmetrization techniques were *not* used for any of the spectra collected. COSY spectra were obtained with use of 19-μs 90° pulses, a 2000-Hz spectral window, 0.256-s acquisition times, and a 1-s relaxation delay; 16 transients were collected for each of 512 t_1 increments. The COSY data were weighted with a shifted sine-bell function and zero-filled to $2k \times 2k$ points before Fourier transformation. NOESY spectra were obtained with use of 19-μs 90° pulses, a 2000-Hz spectral window, 0.256-s acquisition times, a 1.05-s relaxation delay, and 2.0-s mixing time; 16 transients were averaged for each of 512 t_1 increments. The NOESY data were weighted with a shifted sine bell and zero-filled to $2k \times 2k$ points before Fourier transformation.

Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected. Elemental analyses were carried out by Midwest Microlab, Indianapolis, IN.

Preparation of the Complexes. Bis(η^5-tricyclo[5.2.1.0^{2,6}]-deca-2,5,8-trien-4-yl)titanium Dichloride. A solution of the triene (1 g, 7.69 mmol) in 3.3 mL of THF was treated dropwise with *n*-butyllithium in hexane (3.4 mL, 8.1 mmol) at −78 °C under nitrogen. The mixture was stirred at −78 °C for 0.5 h and then allowed to warm to room temperature. The solution was again cooled to −78 °C and added slowly to a solution of $TiCl_4$ (0.42 mL, 3.85 mmol) in THF (0.7 mL)/benzene (2 mL). The reaction mixture was stirred 20 min at room temperature, and the solvent was removed under high vacuum. The remaining red solid was taken up in 20 mL of methylene chloride and shaken with 5% aqueous, ice-cold, HCl. The aqueous layer was extracted with three 15-mL aliquots of methylene chloride, which were combined and dried over anhydrous sodium sulfate. The solvent was evaporated, and the remaining red solid was dissolved in a minimum amount of hot toluene. The solution was kept overnight in a refrigerator at 4 °C, to yield a red powder. This crystallization procedure was repeated with the mother liquor to give a total of 0.78 g (54% yield) of the final compound. Anal. Calcd for $C_{20}H_{18}TiCl_2$: C, 63.67; H, 4.77; Cl, 18.83. Found: C, 63.7; H, 4.80; Cl, 18.74.

Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,5,8-trien-4-yl)zirconium Dichloride. In this preparation, 0.9 g (3.85 mmol) of zirconium tetrachloride was used; otherwise, the synthetic procedure was analogous to that described above for the Ti complex. The final product was obtained in 44% yield (0.71 g). Anal. Calcd for

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[1] Hsu, L.-Y.; Hathaway, S. J.; Paquette, L. A. *Tetrahedron Lett.* **1984**, *25*, 259.

[2] Paquette, L. A.; Schirch, P. F. T.; Hathaway, S. J.; Hsu, L.-Y.; Gallucci, J. C. *Organometallics* **1986**, *5*, 490.

[3] Gallucci, J. C.; Gautheron, B.; Gugelchuck, M.; Meunier, P.; Paquette, L. A. *Organometallics* **1987**, *6*, 15; **1989**, *8*, 573.

[4] Quoted in ref 1.

[5] Bhide, V.; Rinaldi, P.; Farona, M. F. Submitted for publication in *J. Organomet. Chem.*

[6] Alder, K.; Flock, F. H.; Janssen, P. *Chem. Ber.* **1956**, *89*, 2689.

[7] Katz, T. J.; Rosenberger, M.; O'Hara, R. K. *J. Am. Chem. Soc.* **1964**, *80*, 249.

[8] Bodenhausen, G.; Freeman, R.; Niedermeyer, R.; Turner, D. L. *J. Magn. Reson.* **1977**, *26*, 133.

[9] States, D. J.; Haberkorn, R. A.; Ruben, D. J. *J. Magn. Reson.* **1982**, *48*, 286.

[10] States, D. J.; Haberkorn, R. A.; Ruben, D. J. *J. Magn. Reson.* **1977**, *28*, 29.

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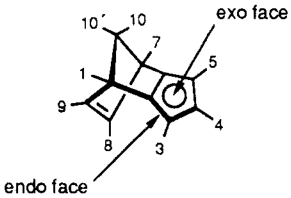
$C_{20}H_{18}ZrCl_2$: C, 57.11; H, 4.28; Cl, 16.90. Found: C, 56.20; H, 4.48; Cl, 16.12. The analytical results from a second sample were comparable; however, NMR spectra do not indicate the presence of any impurities.

Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,5,8-trien-4-yl)hafnium Dichloride. In this case, 1.23 g (3.85 mmol) of $HfCl_4$ was used in a procedure analogous to that described above. The yield of the final product was 0.78 g (40%). Anal. Calcd for $C_{20}H_{18}HfCl_2$: C, 47.29; H, 3.55; Cl, 13.99. Found: C, 46.86; H, 3.58; Cl, 13.85.

Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,5-dien-4-yl)titanium Dichloride. This compound was prepared by using a procedure analogous to that for the bis(trienyl)titanium dichloride complex. It was also prepared by a procedure similar to that of Paquette et al.,[3] wherein the reaction mixture was stirred for 14 h rather than 20 min. In both cases, a product that varied only in isomeric abundance was obtained in 46.4 and 44.4% yields, respectively. Anal. Calcd for $C_{20}H_{22}TiCl_2$: C, 63.01; H, 5.76; Cl, 18.64. Found: C, 62.86; H, 5.79; Cl, 18.38.

Results

Assignment of ^{1}H NMR Resonances and Structure Determination. The discussion that follows on the bis(triene) complexes is based on the numbering system



and abbreviations for exo and endo are used as x and n, respectively. The 300-MHz proton NMR spectrum of $(trienyl)_2ZrCl_2$ indicates a mixture of isomers and is characteristic of the group IV metal chloride complexes studied in this work. Three sets of resonances are clearly identified that can be assigned to *endo,endo*-$(trienyl)_2ZrCl_2$. However, the possibility of an equal mixture of *exo,exo,exo*-$(trienyl)_3ZrCl$ and *exo*-$(trienyl)ZrCl_3$ cannot be eliminated on the basis of the evidence obtained from elemental analysis and the 300-MHz proton NMR spectrum. To elucidate the structure, we resorted to two-dimensional COSY and NOESY experiments. The COSY experiment, which shows correlations of resonances from *J*-coupled protons, permitted us to assign sets of resonances to each chemically nonequivalent ligand. The NOESY experiment, which shows correlations of resonances from protons close enough (3–4 Å apart) to exhibit dipole–dipole interactions, provided information about chemically nonequivalent ligands attached to the same metal ion.

The COSY spectrum (supplementary material) of the $(trienyl)_2ZrCl_2$ isomeric mixture exhibits four correlation regions (A, B, C, and D) and their reflective images relative to the diagonal. Overall correlation information relating the 8/9–1/7, 1/7–10/10′, 10–10′, and 3/4–5 coupling interactions can be obtained from regions A, B, C, and D, respectively. Expansions of these regions (see supplementary material) permit assignment of the resonances to one of the three distinct ligands (nn, x*n*, or *x*n) present in this solution. The ligand coordination stereochemistry is assigned from the NOESY spectra (vide infra) and cannot be obtained from the COSY spectra.

Expansion from the NOESY spectrum of this same $(trienyl)_2ZrCl_2$ isomer mixture is shown in Figure 1. In addition to similar sets of cross-peak patterns found in the COSY spectrum, correlations between 8/9- and 3/4/5-protons (region E, Figure 1a) and 3/4/5- and 1/7-protons (region F, Figure 1b) are found. It is these regions that permit the assignment of ligand coordination stereochemistry and the determination that ligands x*n* and *x*n are part of the same molecules.

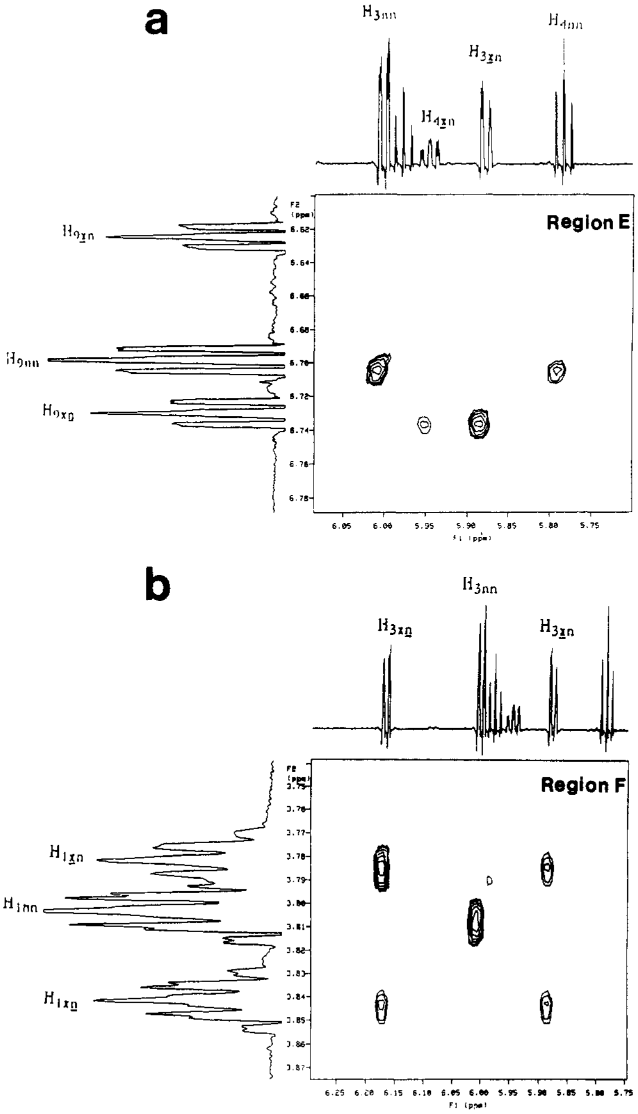


Figure 1. Expansion of regions from the NOESY spectrum of *endo,endo*-$(trienyl)_2ZrCl_2$ and *exo,endo*-$(trienyl)_2ZrCl_2$ showing correlations between (a) $H_{1,7}$ and $H_{3,4,5}$ (region E), and (b) $H_{8,9}$ and $H_{3,4,5}$ (region F). Signals $H_{1x\mathit{n}}$ and $H_{1\mathit{x}n}$ both show cross peaks to the same two ($H_{3x\mathit{n}}$ and $H_{3\mathit{x}n}$) protons in region E. These peaks prove that two of the nonequivalent triene ligands are on the same molecule. Signal H_{1nn} shows a single cross peak to H_{3nn} in region E; therefore, the two ligands in this molecule are equivalent. Signal H_{9nn} exhibits two cross peaks (to H_{3nn} and H_{4nn}) in region F; this can only occur through interligand NOE's since $H_{8,9}$ and $H_{3,4,5}$ are too far apart on the same ligand. Interligand NOE's can only occur between $H_{8,9}$ and $H_{3,4,5}$ if complexation with the metal ion is to the endo face of the Cp ring. Signal $H_{9\mathit{x}n}$ exhibits two cross peaks to resonances $H_{3x\mathit{n}}$ and $H_{4\mathit{x}n}$ in the third set of resonances; therefore, $H_{9x\mathit{n}}$ is from the endo-coordinated ligand in *exo,endo*-$(trienyl)_2ZrCl_2$. $H_{9\mathit{x}n}$ from the *exo*-coordinated ligand does not exhibit cross peaks to resonances in the $H_{3,4,5}$ region, as predicted.

Due to the chemical equivalence of proton resonances from both ligands of *endo,endo*-$(trienyl)_2ZrCl_2$, only one cross peak between H_{1nn}/H_{7nn} and H_{3nn}/H_{5nn} should be observed. However, the chemically nonequivalent ligands of *exo,endo*-$(trienyl)_2ZrCl_2$ will exhibit the two H_1 resonances $H_{1\mathit{x}n}$ and $H_{1x\mathit{n}}$ from the exo- and endo-coordinated ligands, respectively. If these signals are from protons on the same molecule, then they will both show two sets of cross peaks to the same H_3 resonances. $H_{1x\mathit{n}}$ shows cross peaks from intra- and interligand dipole–dipole interac-

Table I. Proton NMR Resonance Assignments for $(trienyl)_2MCl_2$ (M = Ti, Zr, Hf) and $(dienyl)_2TiCl_2$ in $CDCl_3$[a]

	$(trienyl)_2TiCl_2$				$(trienyl)_2ZrCl_2$			
proton	xx	*x*n	x*n*	nn	xx	*x*n	x*n*	nn
1,7	3.86	3.82	3.90	3.86	*b*	3.79	3.85	3.81
3,5	*b*	6.46	6.17	6.26	*b*	5.89	6.18	6.01
4	*b*	6.12	5.95	5.84	*b*	5.96	5.99	5.79
8,9	6.73	6.69	6.55	6.53	*b*	6.63	6.74	6.71
10	2.29	2.24	2.51	2.48	*b*	2.29	2.50	2.46
10′	1.70	1.64	2.40	2.34	*b*	2.02	2.38	2.32

	$(trienyl)_2HfCl_2$					$(dienyl)_2TiCl_2$			
proton	xx	*x*n	x*n*	nn	proton	xx	*x*n	x*n*	nn
1,7	*b*	3.78	3.84	3.80	1,7	3.33	3.29	3.34	*b*
3,5	5.94	5.81	6.09	5.91	3,5	6.07	6.18	6.30	*b*
4	5.99	5.75	5.78	5.58	4	6.26	6.11	5.88	*b*
8,9	6.63	6.59	6.72	6.69	8,9 exo	1.86	1.83	1.86	*b*
10	*b*	2.28	2.60	2.57	8,9 endo	1.10	1.09	1.73	*b*
10′	2.00	1.98	2.36	2.30	10	1.36	1.32	1.92	*b*
					10′	1.21	1.17	1.86	*b*

[a] Resonance assignments were made from 300-MHz COSY and NOESY spectra in all cases; all resonance data are in ppm. [b] Not detected.

tions with $H_{3\mathrm{x}n}$ and $H_{3x\mathrm{n}}$, respectively, and $H_{1x\mathrm{n}}$ shows cross peaks from intra- and interligand dipole–dipole interactions with $H_{3x\mathrm{n}}$ and $H_{3\mathrm{x}n}$, respectively. Therefore, the two sets of resonances labeled *x*n and x*n* are from the same molecule.

Region F of the NOESY spectrum (shown in Figure 1b) allows us to establish the stereochemistry of ligand attachment. Intraligand dipole–dipole interactions between $H_{8,9}$ and $H_{3,4,5}$ are not possible because of the large distance between these protons. NOESY cross peaks can only be observed from interligand dipole–dipole interactions between $H_{8,9}$ of the endo-attached ligand and $H_{3,4,5}$ of an exo- or endo-coordinated ligand attached to the same metal ion. The $H_{9\mathrm{nn}}$ resonance exhibits cross peaks to $H_{3\mathrm{nn}}$ and $H_{4\mathrm{nn}}$, confirming this interaction. The furthest downfield $H_{\mathrm{x}n}$ resonance exhibits cross peaks to $H_{3x\mathrm{n}}$ and $H_{4x\mathrm{n}}$, indicating that the first is H_9 from an *endo*-coordinated ligand and that the last two signals are from the exo-coordinated ligand. $H_{9x\mathrm{n}}$ does not show cross peaks with protons in the $H_{3,4,5}$ region, consistent with the fact that exo-coordinated ligands have $H_{8,9}$ pointed away from the second ligand of the complex, precluding interligand dipole–dipole interactions for these protons.

A summary of the resonance assignments is given in Table I along with the assignments for other complexes of Ti, Zr, and Hf with the triene and diene ligands. These assignments were obtained in a similar manner from COSY and NOESY spectra.

Discussion

The major differences in the preparation of the bis(trienes) in this work and those of the bis(dienes) by Paquette et al. are as follows. For the bis(trienes) the reaction times were 20 min at room temperature for all compounds. For the bis(dienes), the reaction times and temperatures were 14 h at room temperature for the titanium derivative, 70 h at reflux for the Zr compound, and 100 h at reflux for the hafnium complex. In addition, $TiCl_4$ was used in the preparation of $(trienyl)_2TiCl_2$, while $TiCl_3$ served as the starting material for $(dienyl)_2TiCl_2$. Other minor differences were in choice of solvent (THF for the bis(trienes) and dimethoxyethane for the bis(dienes)) and mode of addition of reactants (a solution of the trienyl anion to a solution of MCl_4, and the reverse for the preparation of $(dienyl)_2MCl_2$). In all cases, the yields of the bis(trienes) were somewhat higher than those reported for the corresponding bis(dienes).

For the bis(trienyl)titanium dichloride complex, integration of the corresponding proton signals at the 3,5-positions (see numbering scheme above) revealed an isomeric distribution of 4.3% exo,exo 78.3% exo,endo, and 17.4% endo,endo.

The corresponding zirconium triene complex showed the following isomeric abundances according to NMR integration of the 3,5-proton signals: 0% exo,exo, 38% exo,-endo, and 62% endo,endo. The corresponding hafnium complex gave 1.8% exo,exo, 62.3% exo,endo, and 37% endo,endo.

The bis(trienyl)zirconium dichloride isomeric mixture was refluxed in benzene for 4.5 h to determine whether rearrangement of the exo,endo or endo,endo to the exo,exo configuration might occur. The NMR spectrum showed no change in relative intensities of the proton signals after this treatment, indicating the thermodynamic, rather than kinetic, stabilities of these isomers. This same isomeric mixture was studied by NMR spectroscopy in the −30 to +50 °C temperature range in order to detect any activity that might favor the exo,exo configuration. No change in the relative intensities of the signals was observed over that temperature range.

Whereas it might be thought that the triene ligands do not necessarily follow the same theoretical predictions as the dienes, where only the exo,exo isomers were found with the group IV metals, this certainly is not supported by studies on the ferrocene derivatives of the diene and triene ligands.[5] In that study, the bis(trienyl)iron isomeric distribution was 50% exo,exo, 33% exo,endo, and 17% endo,endo. The bis(dienyl)iron compound showed an isomeric distribution of 75% exo,exo, 18% exo,endo, and 7% endo,endo. Whereas the exo,exo configuration is favored in both cases, particularly in the dienyl compound, it is not formed to the exclusion of the other isomers. With the group IV metals, the exo,exo isomer is formed in very minor amounts in compounds of the trienyl derivatives.

These results prompted a study of bis(dienyl)titanium dichloride. Using extended reaction times for the preparation of $(dienyl)_2MCl_2$ (M = Ti, Zr, Hf) compounds, Paquette et al. obtained exclusively the exo,exo isomer from all three metals. However, from the product obtained from the 20-min preparation of bis(dienyl)titanium dichloride, integration of the 3,5-proton signals in its ^1H NMR spectrum revealed the isomeric distribution to be 26% exo,exo, 68.5% exo,endo, and 5.4% endo,endo. When this same reaction was carried out for 14 h, the product obtained showed an isomeric distribution, as revealed by integration of the 3,5-proton signals in its NMR spectrum, of 40.4% exo,exo, 58.6% exo,endo, and 1% endo,endo.

In the synthesis of the group IV metallocene dichlorides with the triene, we have found that the exo,exo isomer either is not formed at all or is present only in trace amounts. With bis(dienyl)titanium chloride, there appears to be a shift in isomeric distribution toward the exo,exo configuration with longer reaction times, but the major constituent is still the exo,endo, rather than the expected exo,exo, isomer.

We cannot explain the apparent disparity of results between the two studies. However, theory predicts that the exo,exo isomer should be formed, particularly in the titanium case, regardless of the method of preparation, unless a kinetically favored isomer is formed from one preparation and the thermodynamically stable isomer is produced from another. Since we have shown that in the titanium case the major constituent is the exo,endo isomer regardless of the time of reaction and that the bis(trienyl)zirconium complex does not change in isomeric distribution after 4.5 h at reflux temperatures, the possibility that kineticaly favored isomers are produced in this work can be ruled out. Hence, it appears that calculations predicting electronic control of stereochemistry for organic reactions may not apply strictly to organomeallic compounds.

Acknowledgment. We wish to express our appreciation to the State of Ohio for funds from an Academic Challenge grant to acquire the 300-MHz NMR instrument used to perform these studies, and we wish to thank D. Ray and Dr. M. Tokles for obtaining some of the NMR spectra.

Supplementary Material Available: A complete set of ^1H, ^{13}C, COSY, and NOESY NMR spectra of the compounds prepared in this work (44 pages). Ordering information is given on any current masthead page.

Preparation of Sulfur Ylide Complexes of Palladium by Phase-Transfer Catalysis

Rey F. Wu,[†,‡] Ivan J. B. Lin,*[,‡] G. H. Lee,[§] M. C. Cheng,[§] and Yu Wang*[,§]

Departments of Chemistry, Fu Jen Catholic University, Hsin Chuang 24205, Taiwan, and National Taiwan University, Taipei 10764, Taiwan

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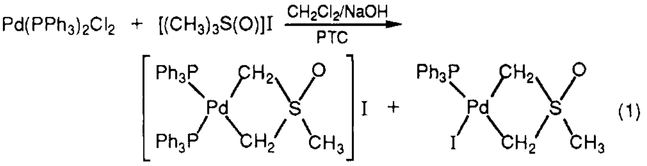
Sulfur ylide complexes of palladium were prepared under basic phase-transfer catalysis. Increasing the amount of phase-transfer catalyst enhanced the rates of formation of the complexes. The optimal range of base concentration was found to be 1.0–2.0 N. The proposed role of the phase-transfer catalyst is to carry OH^- into the organic layer and to prevent the ylide from abstracting a proton from water present in the organic phase. The single-crystal structures of $\{Pd(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$ and $Pd(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ were determined. The former crystallized in the monoclinic space group $P2_1/n$, with $a = 11.337$ (2) Å, $b = 21.954$ (3) Å, $c = 15.406$ (2) Å, $\beta = 94.30$ (1)°, $V = 3823.6$ Å^3, $Z = 4$, and $R = 0.095$ for 4906 observed reflections. The latter crystallized in the orthorhombic space group $P2_12_12_1$, with $a = 9.691$ (3) Å, $b = 14.579$ (2) Å, $c = 15.642$ (3) Å, $V = 2209.9$ Å^3, $Z = 4$, and $R = 0.078$ for 2201 observed reflections. Both compounds have rather short ylidic S–C bonds (1.60–1.70 Å).

Introduction

Phase-transfer catalysis (PTC) has been widely applied in organic chemistry.[1-4] In contrast, there have been relatively few examples in organometallic chemistry,[5-11] the first being reported in 1976.[10] The application of the PTC technique to organometallic synthesis is even rarer.[12-17] In a previous communication,[16] we have shown that palladium sulfur ylide complexes 1 and 2 were obtained in high yields by the reaction of trimethylsulfoxonium iodide with $Pd(PPh_3)_2Cl_2$ under basic PTC conditions (eq 1). This PTC reaction is unusual in view of the known instability of sulfur ylides in anhydrous solvents at room temperature.[18] In comparison, a reaction has been carried out in dry THF under N_2 and with NaH as the base, and we have shown that the PTC/OH^- technique has the following advantages: anhydrous conditions are not required; relatively high yields of complexes are obtained; a cheap and easily used base, NaOH, can be used. In a subsequent paper,[19] it was shown that sulfur ylide complexes of palladium, zinc, and copper can be formed even in water. In another work[20] it was demonstrated that under PTC conditions both the reaction rates and yields (eq 2) of mixed-ligand complexes were enhanced. In this paper, we report our continued


$Pd(PPh_3)_2Cl_2 + [(CH_3)_3S(O)]I \xrightarrow[PTC]{CH_2Cl_2/NaOH}$

(1)

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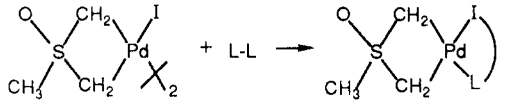
(2)

L-L = 1,1-dithiolates, acetylacetonate

[†] Deceased January 29, 1987.

[‡] Fu Jen Catholic University.

[§] National Taiwan University.

(1) Weber, W. P.; Gokel, G. W. *Phase Transfer Catalysis in Synthesis*; Springer-Verlag: West Berlin, 1977.

(2) Starks, C. M.; Liotta, C. *Phase Transfer Catalysis-Principles and Techniques*; Academic Press: New York, 1978.

(3) Montanari, F.; Landidi, D.; Rolla, F. *Top Curr. Chem.* **1982**, *101*, 147.

(4) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*, 2nd ed.; Verlag Chemie: Weinheim, FRG, 1983.

(5) Cassar, L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 208.

(6) Alper, H. *Adv. Organomet. Chem.* **1981**, *19*, 183.

(7) Tanguy, G.; Weinberger, B.; des Abbays, H. *Tetrahedron Lett.* **1983**, *24*, 4005; **1984**, *25*, 5529.

(8) des Abbayes, H. *Isr. J. Chem.* **1985**, *26*, 249.

(9) Alper, H. In *Phase Transfer Catalysis, New Chemistry, Catalysts, and Applications*; Starks, C. M., Ed.; ACS Symposium Series 326; American Chemical Society: Washington, DC, 1987.

(10) Alper, H.; des Roches, D. *J. Organomet. Chem.* **1976**, *117*, C44.

(11) des Abbayes, H.; Clement, J.-C.; Laurent, P.; Tanguy, G.; Thilmont, N. *Organometallics* **1988**, *7*, 2293.

(12) Gibson, D. H.; Hsu, W. L.; Lin, D. S. *J. Organomet. Chem.* **1979**, *172*, C7.

(13) Bhaduri, S.; Sharma, K. R. *J. Organomet. Chem.* **1981**, *218*, C37.

(14) des Abbayes, H.; Buloup, A.; Tanguy, G. *Organometallics* **1983**, *2*, 1730.

(15) Weinberger, B.; Tanguy, G.; des Abbayes, H. *J. Organomet. Chem.* **1985**, *280*, C31.

(16) Lin, I. J. B.; Lai, H. Y. C.; Wu, S. C.; Hwan, L. *J. Organomet. Chem.* **1986**, *304*, C24.

(17) Tanguy, G.; Clement, J.-C.; des Abbayes, H. *J. Organomet. Chem.* **1986**, *314*, C43.

(18) Trost, B. M.; Melvin, L. S., Jr. *Sulfur Ylide*; Academic Press: New York, 1975; p 23.

0276-7333/90/2309-0126$02.50/0