Structural Organometallic Chemistry and its Relation to Homogeneous Catalysis

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Abstract: A useful aid in enantioselective homogeneous catalysis, new chiral complexes based on phosphorus acid and a novel approach to recognizing ion-pairing are described.

Keywords: Diffusion · Enantioselective homogeneous catalysis · Ion-pairing · Organometallic chemistry

Introduction

Although homogeneous catalysis and, specifically, enantioselective catalysis, continues to attract an increasing audience, the correct selection of chelating auxiliary still represents a major challenge. Experience has taught us that no single bidentate phosphine, oxazoline or diol (or even mixtures of donor ligands within an auxiliary), provides a perfect chiral pocket for all substrates and reactions. Further, the catalysis community is constantly in need of new (or new applications of existing) analytical methods to assist in understanding how metal catalyzed reactions proceed.

The research activities in our group revolve around structural organometallic chemistry and its relevance to homogeneous catalysis. Within this area there are three subgroups: i) those concerned directly with enantioselective homogeneous catalysis and specifically palladium catalyzed reactions ii) synthetic ruthenium chemistry designed to access new ligands and iii) applications of NMR spectroscopic methods to the above problems.

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Enantioselective Heck Reaction Using MeO-Biphep Ligands: 3,5-Dialkylphenyl Substituents and the Case Against Dibenzylidene Acetone

In recent years we have shown [1] that the Pd-catalyzed enantioselective Heck reaction of p-XC$_6$H$_4$OTf, X = OMe, H, CO$_2$Me with dihydrofuran derivatives affords higher enantioselectivity when the chelating diphosphine, MeO-Biphep **1a**, is replaced with its *meta* disubstituted analog 3,5-di-t-butyl MeO-Biphep **1b**.
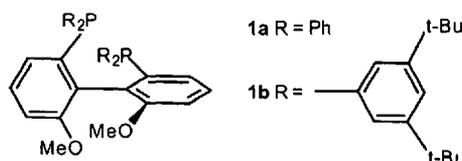
The phenylation of 5-methyl-2,3-dihydrofuran is a useful, if dramatic example of this effect (Scheme 1):
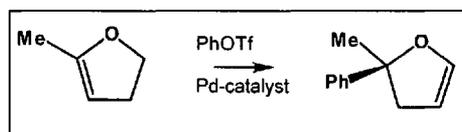
Scheme 1. With **1a**; ee = ca. 20%, with **1b**; ee = > 98%

There is reason to believe that this type of observation has some generality as related results are known in hydrogenation chemistry with Ru [2], Ir [2] and Rh [3] complexes. The source of the effect lies in the increased rigidity of the chiral pocket due to selective restricted rotation [1][4–6].

Apart from catalytic results, we noted that for the catalyzed reaction of phenyl triflate with dhf, as well as for stoichio-

metric oxidative addition reactions of aryl halides on Pd-complexes of **1**, the use of Pd(dba)(**1**), dba = dibenzylidene acetone, slows the oxidative addition relative to the reaction in which the Pd(0) precursor is generated from PdCl$_2$(**1**) + NaBH$_4$ (Scheme 2).

Equations (1)-(4) indicate this chemistry and Fig. 1 represents the development of organic product as a function of time using several catalyst precursors. The catalytic reactions were carried out at 313K, but the experiments for the relative kinetics, at room temperature, to facilitate monitoring by NMR methods. From Fig. 1 it can be seen that the complexes PdCl$_2$(**1a** or **1b**) slowly catalyze the reaction, but the dba complex is hardly active. Since some organic substrates will not tolerate reaction at elevated temperature, the correct choice of catalyst precursor can be critical. With the dba precursor at ambient temperature, there is, practically speaking, no reaction. It is surprising that, relatively speaking, dba still enjoys considerable popularity in palladium chemistry.

Alcohol Induced Stereospecific P-C Bond Cleavage to Afford Ru-Phenyl Derivatives Containing Three Different Types of Stereogenicity

In the course of studying [7] the hydrogenation precursor Ru(OAc)$_2$(Binap) (**2**) we have prepared the new complexes **3** [8] and **4** [9] shown in Scheme 3. These are interesting new ruthenium complexes in that they are produced in *only one diastereomeric form* (note that the metal

represents a stereogenic center). Moreover, the phenyl migration from **3** to **4** and P–O bond formation are specific. Further, complex **4** contains *three different forms of stereogenicity*. These arise from the biaryl moiety, a chiral transition metal and the newly formed stereogenic P-atom. These are the first reported transition metal complexes of the ligands P(OH)(OR)Ph and potentially open new possibilities in organometallic phosphorus chemistry.

Applications of Pulsed Gradient Spin Echo (PGSE) Diffusion Measurements to Organometallic Chemistry

Diffusion data from Pulsed Field Gradient Spin-Echo (PGSE) methods are routine in several areas of chemistry [10][11], but exceedingly rare in organometallic chemistry [12–14]. We have recently shown this method to be qualitatively useful in the investigation of problems involving unknown molecular aggregation [15][16] and/or the nature of inter-ionic interactions in metal complexes [17]. For cationic ruthenium (and palladium and rhodium, *etc.*) catalyst precursors containing anions such as PF_6^-, BF_4^-, $CF_3SO_3^-$ or $BArF^-$, *both* ^{19}F and ^1H PGSE methods offer a valid alternative and sometimes unique view of gross and subtle solution molecular structure and dynamics. For these complexes, ^{19}F represents both an alternative and a complement to ^1H PGSE methods so that one can determine the diffusion constants for the metal cation and main-group anion separately and thus investigate ion-pairing. In this connection, an interesting and unexpected solvent dependence was obtained from PGSE measurements on the ruthenium arene PF_6^- salt **5**, and the palladium allyl-complex **6**.
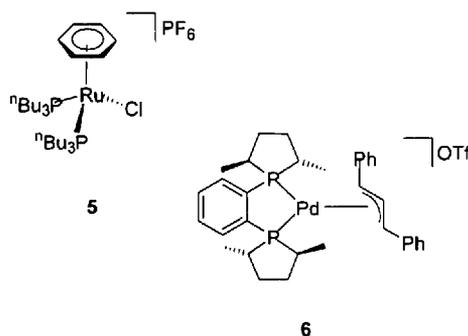
The Table shows results in $CDCl_3$ and CD_2Cl_2, for both the cation and the counter-ion (using the ^1H and ^{19}F resonances respectively), with Fig. 2 providing a visual aid for **5**.

Pd(dba)(**1a**) + PhOTf + dhf	$\rightarrow$ acetone, 40 °C	no reaction after 72 h	(1)
PdCl$_2$(**1a**) + PhOTf + dhf	NaBH$_4$ $\rightarrow$ acetone, 40 °C	70% conversion after 42 h	(2)
Pd(dba)(**1b**) + PhOTf + dhf	$\rightarrow$ acetone, 40 °C	no reaction after 72 h	(3)
PdCl$_2$(**1b**) + PhOTf + dhf	NaBH$_4$ $\rightarrow$ acetone, 40 °C	44% conversion after 67 h	(4)
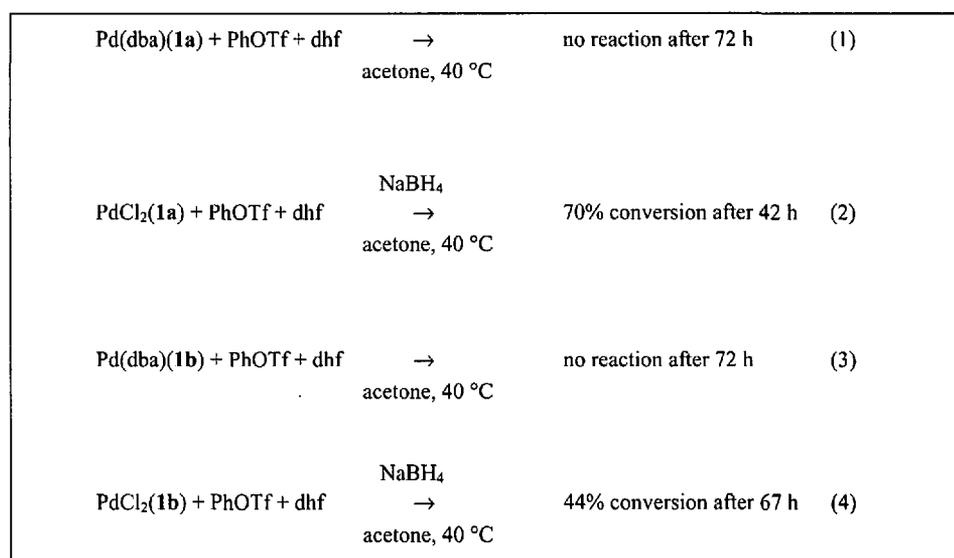
Scheme 2.
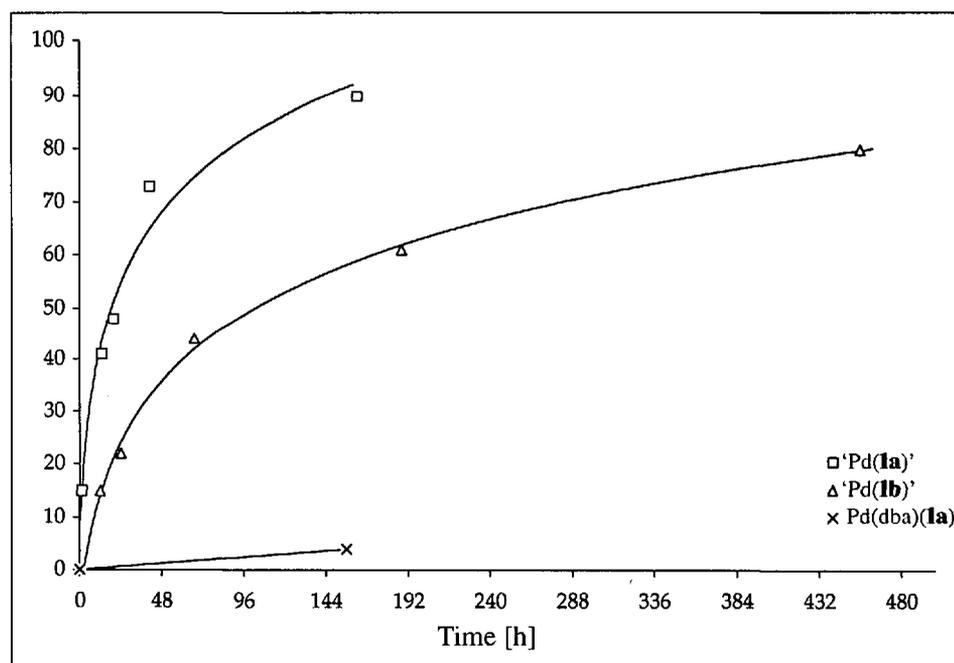
Fig. 1. Development of the 2-phenyl furan organic product as a function of time, for the Pd-catalyzed Heck reaction of dhf with PhOTf. The upper curves arise from the reactions of 'Pd(**1a**)' (fastest) and 'Pd(**1b**)', whereas the bottom curve shows that little product is formed from Pd(dba)(**1a**) after *ca.* 100 h.

5

6
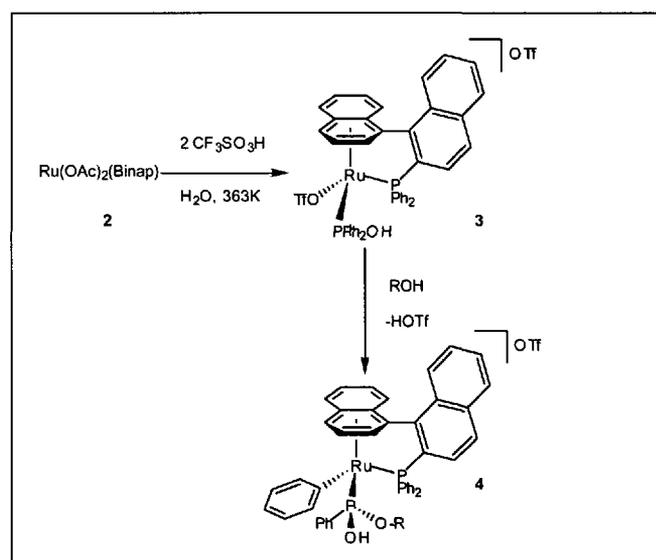
Scheme 3.

While the two lines for the CD_2Cl_2 solution show different slopes, those in $CDCl_3$ are so close that one can barely resolve them. Both complexes exist as tight ion pairs in chloroform, with the positive fragment and counter-ion revealing the same diffusion coefficients, while in methylene chloride solution, the cationic and anionic fragments are moving at different rates. The dielectric constant and dipole moment for methylene chloride are both larger than the corresponding values for chloroform, thus partially rationalizing these observations. This methodology is clearly a promising tool where anionic effects on catalytic reactions are observed.

These studies in catalysis, organometallic chemistry and NMR spectroscopy stretch across all three of the classical chemistry disciplines.

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Table. D and r_H values for cation and counterion in $CDCl_3$ and CD_2Cl_2 of 5 and 6

Compound	solvent	fragment	10^{10} D[a] [m^2 s^{-1}]	r_H[b] [Å]
5	$CDCl_3$	cation[c]	6.25 (6)[d]	6.3 (1)[d]
	$CDCl_3$	PF_6^- [e]	6.27 (6)	6.3 (1)
	CD_2Cl_2	cation[c]	8.74 (6)	6.2 (1)
	CD_2Cl_2	PF_6^- [e]	10.17 (6)	5.3 (1)
6	$CDCl_3$	cation[c]	6.64 (6)	6.0 (1)
	$CDCl_3$	OTf$^-$ [e]	6.45 (6)	6.1 (1)
	CD_2Cl_2	cation[c]	9.14 (6)	5.9 (1)
	CD_2Cl_2	OTf$^-$ [e]	11.69 (6)	4.7 (1)

[a]) Estimated using the diffusion coefficient of HDO in D_2O as reference.
[b])Calculated using a viscosity value for $CDCl_3$ and CD_2Cl_2 equal to 0.55 10^{-3} and 0.40 10^{-3} kg s^{-1} m^{-1}, respectively.
[c]) Using ^1H signals.
[d]) Standard deviation.
[e]) Using ^{19}F resonance.

Fig. 2. Effect of the polarity of the solvent on 5. Left, are the two lines (^1H and ^{19}F) for 5 in $CDCl_3$. They are strongly overlapped. Right, in the inset, are the analogous data (^1H and ^{19}F) from 5 in CD_2Cl_2. Clearly, in CD_2Cl_2, the cation and anion are moving separately. ^{19}F results are corrected for the contribution of the gyromagnetic ratio of fluorine. The spin-echo signal intensities (and thus the slopes) decrease faster for smaller molecules.

[1] G. Trabesinger, A. Albinati, N. Feiken, R.W. Kunz, P.S. Pregosin, M. Tschoerner, J. Am. Chem. Soc. 1997, 119, 6315; M. Tschoerner, P.S. Pregosin, A. Albinati, Organometallics 1999, 18, 670; K. Selvakumar, M. Valentini, P.S. Pregosin, A. Albinati, F. Eisentraeger, Organometallics 2000, 19, 1299.

[2] E.A. Broger, W. Burkhart, M. Hennig, M. Scalone, R. Schmid, Tetrahedron Asymmetry 1998, 9, 4043 and references therein; R. Schmid, E.A. Broger, M. Cereghetti, Y. Crameri, J. Foricher, M. Lalonde, R.K. Mueller, M. Scalone, G. Schoettel, U. Zutter, Pure & Appl. Chem. 1996, 68, 131.

[3] T.V. Rajanbabu, T.A. Ayers, A.L. Caasalnuovo, J. Am. Chem. Soc. 1994, 116, 4101.

[4] P.S. Pregosin, M. Valentini, Enantiomer 1999, 4, 529.

[5] P.S. Pregosin, G. Trabesinger, J. Chem. Soc. Dalton Trans. 1998, 727.

[6] P.S. Pregosin, H. Ruegger, R. Salzmann, A. Albinati, F. Lianza, R.W. Kunz, Organometallics 1994, 13, 83.

[7] A. Currao, N. Feiken, A. Macchioni, R. Nesper, P.S. Pregosin, G. Trabesinger, Helv. Chim. Acta 1996 79, 1587; N. Feiken, P.S. Pregosin, G. Trabesinger, A. Albinati, G.L. Evoli, Organometallics 1997, 16, 5756; N. Feiken, P. S. Pregosin, G. Trabesinger, Organometallics 1997, 16, 3735; N. Feiken, P.S. Pregosin, G. Trabesinger, M. Scalone, Organometallics 1997, 16, 537.

[8] C. J. den Reijer, H. Rüegger, P.S. Pregosin, Organometallics 1998, 17, 5213.

[9] T.J. Geldbach, D. Drago, P.S. Pregosin, Chem. Commun. 2000, 1629.

[10] W.S. Price, Ann, Rep. NMR Spectrosc. 1996, 32, 51.

[11] P. Stilbs, Prog. NMR Spectr. 1987, 19, 1.

[12] C.B. Gorman, J.C.J. Smith, M.W. Hager, B.L. Parkhurst, H. Sierzputowska-Gracz,

C.A. Haney, J. Am. Chem. Soc. 1999, 121, 9958; S. Beck, A. Geyer, H.H. Brintzinger, Chem. Commun. 1999, 2477.

[13] B. Olenyuk, M.D. Lovin, J.A. Whiteford, P.J.J. Stang, J. Am. Chem. Soc. 1999, 121, 10434.

[14] R.M. Stoop, S. Bachmann, M. Valentini, A. Mezzetti, Organometallics 2000, 19, 4117.

[15] A. Pichota; P.S. Pregosin, M. Valentini, M. Wörle, D. Seebach, Angew. Chem. Int. Ed. 2000, 39, 153.

[16] M. Valentini, P.S. Pregosin, H. Ruegger, J. Chem. Soc. Dalton Trans. 2000, 4507; M. Valentini, P.S. Pregosin, H. Rüegger, Organmetallics 2000,19, 2551.

[17] M. Valentini, P.S. Pregosin, H. Ruegger, Helv. Chim. Acta 2001, submitted.