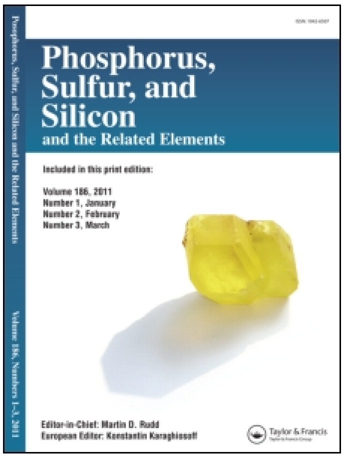
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Control of the Stereochemistry and Electronic Configuration of Transition Metal Complexes by New Tripodalligands

H. A. Mayer[a]
[a] Institut für Anorganische Chemie der Universität Tübingen, Tübingen, W-Germany

To cite this Article Mayer, H. A.(1993) 'Control of the Stereochemistry and Electronic Configuration of Transition Metal Complexes by New Tripodalligands', Phosphorus, Sulfur, and Silicon and the Related Elements, 77: 1, 53 — 56

To link to this Article: DOI: 10.1080/10426509308045617

URL: http://dx.doi.org/10.1080/10426509308045617

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, pp. 53–56
Reprints available directly from the publisher
Photocopying permitted by license only

CONTROL OF THE STEREOCHEMISTRY AND ELECTRONIC CONFIGURATION OF TRANSITION METAL COMPLEXES BY NEW TRIPODAL LIGANDS

HERMANN A. MAYER
Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, W-Germany

Abstract In spite of the C_{3v} symmetry of the new tripodal phosphine ligands **1**,**2** no *facial* coordination to Ir(I) and Ir(III) is observed. **1** forms square planar, square pyramidal, and octahedron iridium complexes with two phosphine "arms" coordinated *trans* to one another. The third phosphine "arm" which remains uncoordinated is in a fast exchange process with the metal bound phosphines. Intramolecular metalation of a C-H bond of the cyclohexane ring occurs when **2** is treated with $Ir(PPh_3)_2(CO)Cl$.

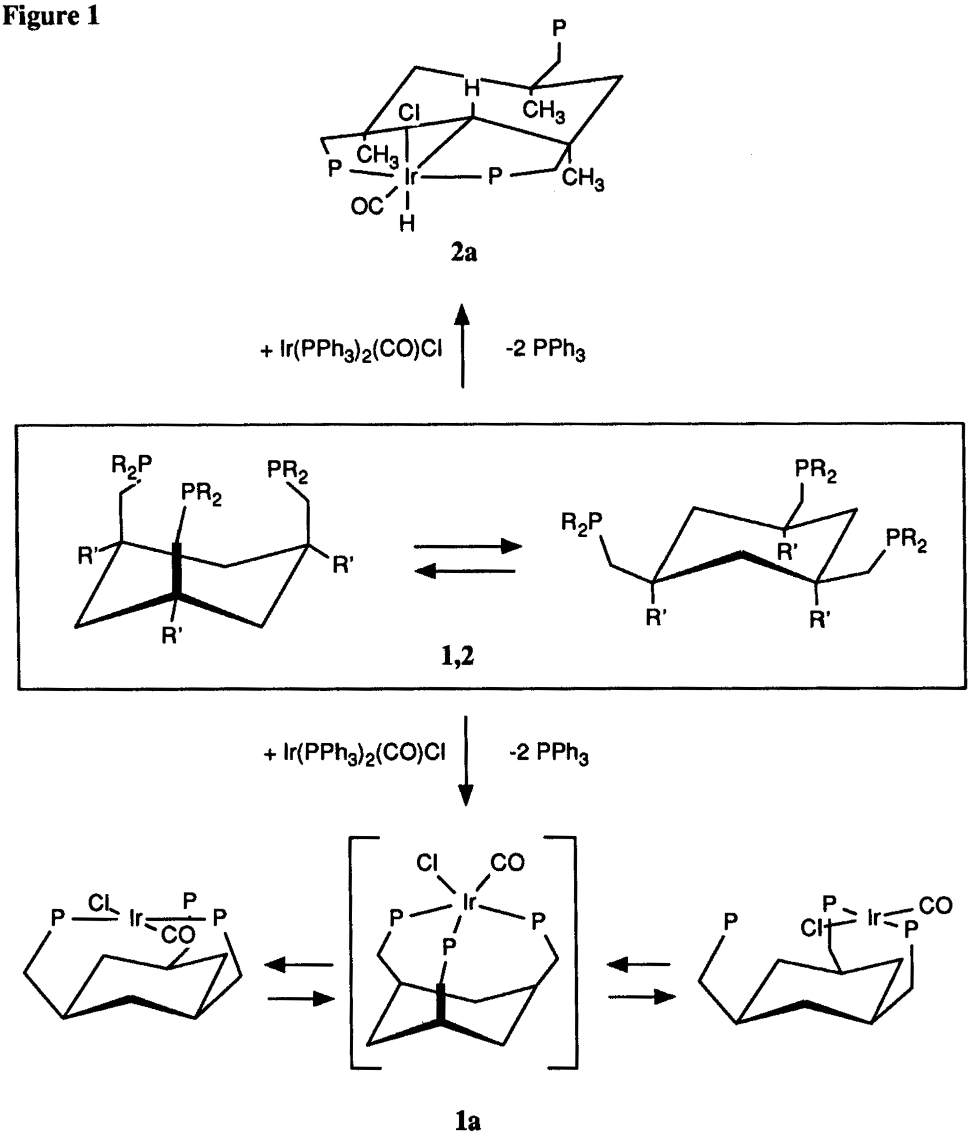
Introduction

Polyphosphines attract considerable interest as ligands which stabilize transition metal complexes. Depending on the nature of the metal and on the design of the polyphosphine, complexes with a variety of coordination geometries can be achieved. Thus it is possible to control the stereochemistry and the electronic configuration of transition metal complexes.[1]

Results and Discussion

In the new tripodal ligands **1**,**2** (**1**: R = Phenyl, R' = H[2]; **2**: R = Phenyl, R' = Methyl; Figure 1) three (diphenylphosphino)methyl groups are specifically bound in *cis,cis*-1,3,5 positions to a cyclohexane ring. Because of the C_{3v} symmetry of the ligands it is expected that a *facial* geometry is adopted when **1**,**2** are coordinated to a trigonal bipyramidal or an octahedron metal center. However, the stereochemistry imposed by **1,2** on a metal center is not only a function of the chelate angle of the phosphines but also depends on the conformation (flexibility) of the cyclohexane ring. For the coordination chemistry it is of further significance, whether the equatorial or axial site will be occupied by the (diphenylphosphino)methyl groups. Therefore in **2** methyl groups were introduced at the *ipso* positions. This dramatically lowers the energie barrier for the equatorial - axial site exchange as was demonstrated by a VT ^{1}H NMR study. While

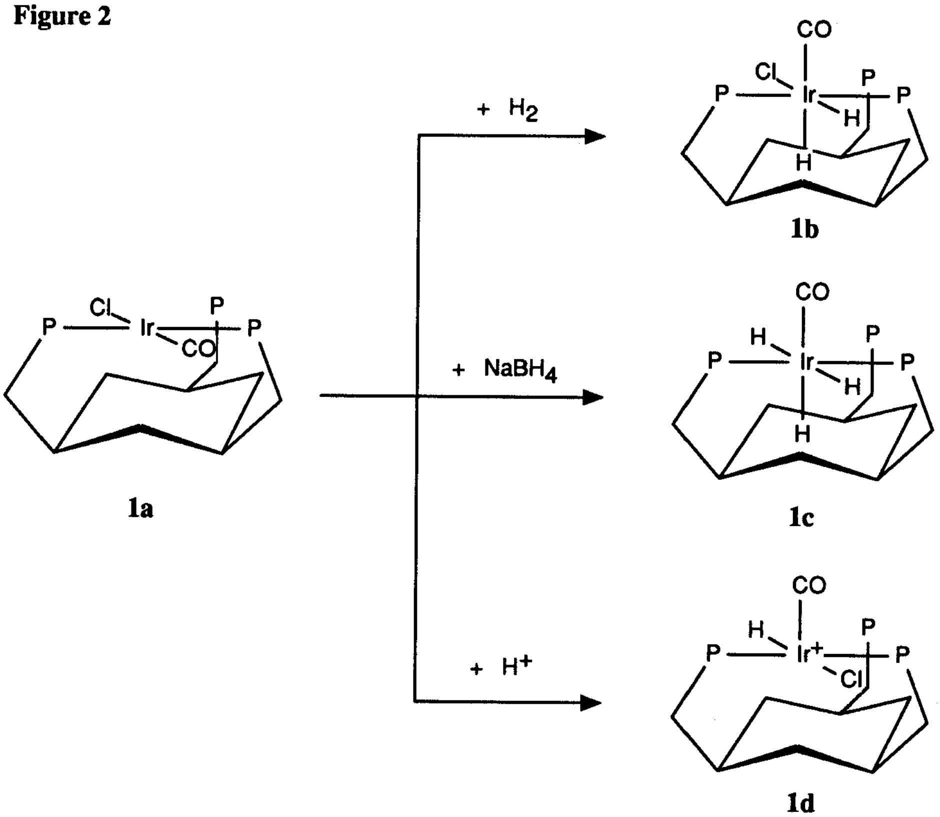
Figure 1



1 shows no line broadening due to an exchange process up to 100 °C a coalescence of the equatorial and axial positions is observed at 72 °C in the case of **2**. A x-ray structure analysis establishes that in the ground state geometry of **2** the methyl groups are in the axial and the sterically more crowded (diphenylphosphino)methyl groups are in the equatorial positions.[3]

When Ir(PPh_3)$_2$(CO)Cl is treated with **1** in toluene PPh_3 is replaced by **1** and a new compound is isolated which on the basis of spectroscopic characterization and reaction chemistry is formulated as shown in Figure 1. A square planar Vaska type complex is

Figure 2



formed with two phosphine groups coordinated *trans* to one another. The third phosphine "arm" remains uncoordinated, however, is in a fast exchange process with the phosphine groups bound to the metal. Like Vaska's complex **1a** reacts reversibly with H_2 at atmospheric pressure to give the pale yellow octahedron Ir(III) dihydride complex **1b** (Figure 2). IR and NMR spectroscopic data are consistent with the *cis* addition of H_2 and thus demonstrates that the stereochemistry at the metal center is the same as that observed in the kinetic product of the H_2 oxidative addition to Vaska's complex.[5] Due to the geometry of the ligand four isomers can be generated which are observed in the ^1H and ^{31}P NMR spectra. The reduction of **1a** with a large excess of $NaBH_4$ leads to the quantitative formation of the *meridional* trihydride complex **1c** (Figure 2). This also demonstrates the similarity to Vaska's complex which results in a *meridional* trihydride, too when reduced with $NaBH_4$.[6] Treatment of **1a** with triflic acid results in the protonation of the metal center producing the square pyramdial complex **1d** (Figure 2). The stereochemistry of the complexes **1a-d** is obtained from their IR, ^1H, ^{13}C, and ^{31}P NMR spectra. In each case the NMR data are consistent with a C_{3v} symmetry of the ligand and thus of a dynamic behavior. In spite of the C_{3v} symmetry of the ligand no *facial* coordination to either Ir(I) or Ir(III) is observed. In square planar (**1a**), square pyramidal (**1d**), and octahedron (**1b,c**) complexes the two phosphines which are coordinated *trans* to one another are involved in a fast exchange process with the third non-coordinated phosphine arm. In each case the cyclohexane ring remains in the chair conformation while the (diphenylphosphino)methyl groups coordinate from the equatorial site. In agreement with **1** ligand **2** also displaces two *trans* PPh_3 groups from Vaska's complex by two (diphenylphosphino)methyl "arms", however, in addition the metal inserts into an equatorial C-H bond of the cyclohexane ring (Figure 1, **2a**). While the C_s symmetry of **2a** could be deduced from the IR, ^1H, ^{13}C, and ^{31}P NMR spectra, the metalation of the equatorial C-H bond was established by a x-ray diffraction analysis.

Support of this work by Deutsche Forschungsgemeinschaft, Bonn/Bad Godesberg and by Degussa AG is gratefully acknowledged.

References

1. R. Mason and D. W. Meek, Angew. Chem., 90, 195 (1978); Angew. Chem. Int. Ed. Engl., 17, 183 (1978).
2. H. A. Mayer and W. C. Kaska, Chem. Ber., 123, 1827 (1990).
3. H. A. Mayer, R. Fawzi and M. Steimann, Chem. Ber., in preparation.
4. H. A. Mayer, Organometallics, in preparation.
5. P. L. Deutsch and R. Eisenberg, Chem. Rev., 88, 1147 (1988).
6. J. F. Harrod and W. J. Yorke, Inorg. Chem., 20, 1156 (1981).