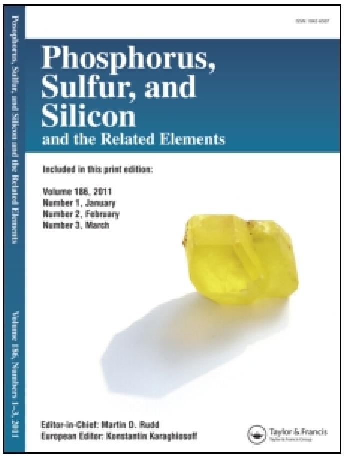

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Phosphinothioformamides - A Class of Versatile Ambidentate Complex Ligands

Udo Kunze[a]; Andreas Bruns[a]; Hussain Jawad[a]
[a] Institut für Anorganische Chemie, Universität Tübingen Auf der Morgenstelle 18, Tübingen

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PHOSPHINOTHIOFORMAMIDES - A CLASS OF VERSATILE AMBIDENTATE COMPLEX LIGANDS

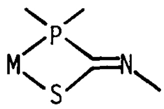
UDO KUNZE*, ANDREAS BRUNS and HUSSAIN JAWAD

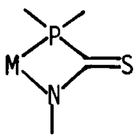
Institut für Anorganische Chemie, Universität Tübingen
Auf der Morgenstelle 18, D-7400 Tübingen

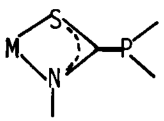
Abstract Secondary and tertiary phosphinothioformamides have proved to be flexible, ambidentate complex ligands. Structural differences in solid and dissolved state have been made observable by carbon-13 CP-MAS NMR techniques. The $(CO)_4M(\overset{\frown}{PS})$ complexes (M = Cr, Mo, W) react with monodentate ligands under reversible fission of the metal-sulfur bond which favours the application of such systems in metal-catalyzed syntheses. We suggest three ways for the preparation of chiral phosphinothioformamides which show a high diastereoselectivity upon coordination to prochiral half-sandwich complexes.

INTRODUCTION

Secondary phosphinothioformamides, $R^1_2PC(S)NHR^2$, and the corresponding thioformimidate anions were applied for the complexation of metals in different coordination number and configuration. Investigations were carried out with square-planar (Rh, Ir, Pt), tetrahedral (Fe), square-pyramidal (Mo, W) and octahedral (Mn, Re) systems[1]. Three fundamental coordination modes are available for the "heterocarbonate" ligands (shown for anionic species):







STEREOCHEMISTRY OF THE LIGANDS

Structural differences in solid and dissolved state were investigated by ^{13}C-CP-MAS NMR spectroscopy[2]. We found an asymmetric signal splitting of the carbon atoms bound to nitrogen due to quadru-

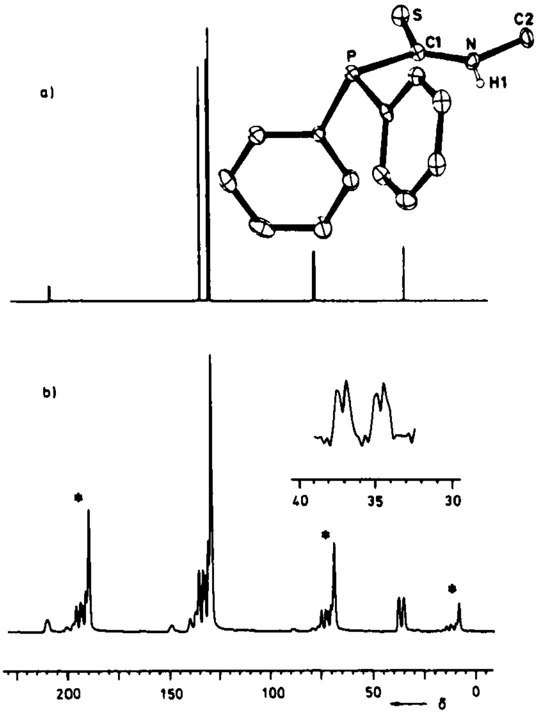


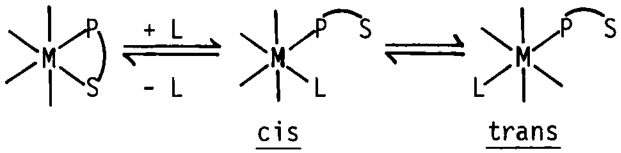
FIGURE 1 a. Crystal structure (molecule 1) and $^{13}C\{^1H\}$-NMR spectrum ($CDCl_3$), b. ^{13}C-CP-MAS NMR spectrum (* rotational side bands) of $Ph_2PC(S)NHMe$.

pole interaction. The solid state ^{13}C-NMR spectrum of $Ph_2PC(S)NHMe$ shows two signals in the N-methyl range which correspond to two symmetry-independent (*Z*) molecules in the asymmetric unit (Fig. 1).

Solid tertiary phosphinothioformamides, $R^1_2PC(S)NR^2R^3$, and the linkage-isomeric S-alkyl thioformimidoesters, $R^1_2PC(NR^2)SR^3$, adopt *Z* configuration with respect to the central CN bond[3]. In solution, *E*/*Z* isomerisation is observed with P-oxides and -sulfides. The free energies of activation amount to 70 - 90 kJ·mol^{-1}.

COORDINATION CHEMISTRY

A series of tetracarbonyl chelate complexes with neutral thioformamide ligands was prepared by low-temperature photolysis of the metal hexacarbonyls, $M(CO)_6$ (M = Cr, Mo, W)[4]. In contrast to the

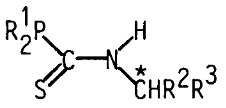


(M = Cr,Mo,W)

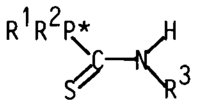
thioformimidate complexes, $(CO)_4M(\overset{\frown}{PS})$ (M = Mn, Re), the substitution with Group VB ligands proceeds without CO elimination but reversible cleavage of the metal-sulfur bond and cis-trans isomerisation. The rechelatisation is influenced by temperature, solvent and light. Ideal reversible conditions are encountered with the N,N-dimethylthioformamide ligand which completely reverts to the chelate complex without isomerisation. This favours the application of such systems in metal-catalyzed syntheses.

CHIRAL LIGANDS AND DIASTEREOSELECTIVE COMPLEXATION

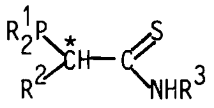
We have suggested three ways for the introduction of an asymmetric centre at carbon or phosphorus[5]:



I, N-C* chiral



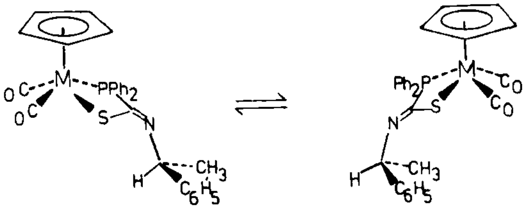
II, P* chiral



III, P-C* chiral

Type I ligands were obtained from optically pure amines and amino acids. By reaction with $CpM(CO)_3Cl$ (M = Mo, W) in methanol, the insoluble diastereomer of the P,S-coordinated complexes is precipitated in pure form. In solution, epimerisation to a 1/1 diastereomeric equilibrium is observed which follows a formal first-order kinetics with $\Delta G^{\ddagger} = 92 \pm 5$ kJ·mol^{-1} at T = 20 - 40°C.

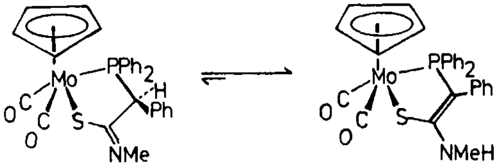
In contrast, the stereoselective formation of the S,N-coordinated P=O complexes proceeds under homogeneous conditions and is favoured by thermodynamics. The S,S-coordinating P=S ligands do not show any selectivity. Complexes derived from R(+)- and S(-)-1-phenylethylamine are enantiomeric and give mirror-symmetrical CD plots.



1a,b

M=Mo: $[\alpha]_D^{20} = +140{,}1°$

M=W: $[\alpha]_D^{20} = +83{,}2°$ (Lsg. Toluol)



Mixed phosphine ligands of type II coordinate with a high extent of optical induction depending on the size of the P substituents and the metal. Type III ligands were obtained by nucleophilic addition of phosphinomethanide carbanions to isothiocyanate but proved to be unapt for the stereoselective synthesis since a rearrangement to the tautomeric enamine form takes place upon complexation.

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REFERENCES

1. Survey: A. Antoniadis, U. Kunze and M. Moll, J. Organomet. Chem., 235, 177 (1982).
2. K. Albert, A. Bruns, H. Förster, W. Hiller and U. Kunze, Angew. Chem., 97, 687 (1985); Int. Ed. Engl., 24, 715 (1985).
3. U. Kunze, A. Bruns, W. Hiller and J. Mohyla, Chem. Ber., 118, 227 (1985).
4. U. Kunze and H. Jawad, J. Organomet. Chem., 277, C31 (1984).
5. U. Kunze, H. Jawad, R. Burghardt, R. Tittmann and V. Kruppa, J. Organomet. Chem., 302, C30 (1986).