Inorganic Chemistry

Communication

pubs.acs.org/IC

Synthesis and Characterization of a New Binucleating Tetraphosphine Ligand Based on 1,2-Phenylene Chelates and the Structures of Dinickel Tetrachloride Complexes of the Ligand

William J. Schreiter, Alexandre R. Monteil, Ekaterina Kalachnikova, Marc A. Peterson, Marshall D. Moulis, Ciera D. Gasery, Gregory T. McCandless, Frank R. Fronczek, and George G. Stanley*

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804, United States

S *Supporting Information*

ABSTRACT: A new binucleating tetraphosphine ligand, *rac-* and *meso-*$(Et_2P\text{-}1,2\text{-}C_6H_4)P(Ph)CH_2(Ph)P(1,2\text{-}C_6H_4PEt_2)$ (et,ph-P4-Ph), has been synthesized. Separation and purification of the ligand diastereomers have been accomplished via column chromatography. Ni_2Cl_4(et,ph-P4-Ph) complexes of both diastereomers have been prepared in high yield and crystallographically characterized.

The tetraphosphine ligands *rac-* and *meso-*$(Et_2PCH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PEt_2)$ (et,ph-P4), **1R** and **1M** (Figure 1), were designed to bridge and chelate two metal centers to promote bimetallic cooperativity during a catalytic reaction.[1,2] This goal was realized with the synthesis of $[Rh_2(nbd)_2(\textit{rac}\text{-et,ph-P4})][BF_4]_2$ (nbd = norbornadiene), which is a precursor to a very active and regioselective hydroformylation catalyst.[3−5] This catalytic system remains one of the most dramatic examples of bimetallic cooperativity in homogeneous catalysis.

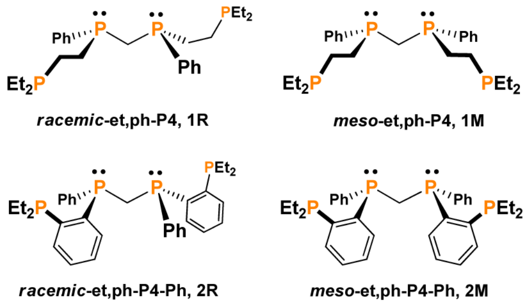


Figure 1. (Top) Tetraphosphine ligands **1R** and **1M**. (Bottom) New more strongly chelating tetraphosphine ligands **2R** and **2M**.

Spectroscopic studies[4,6−8] on the dirhodium system as well as on a related nickel system[9] have shown that these complexes can, unfortunately, readily fall apart to form inactive mono- and bimetallic complexes (Figure 2). This is likely due to the rotational flexibility of the ethylene bridge, which allows one of the PEt_2 arms to dissociate, leading to the loss of a metal center, even under mild conditions. Once one metal center is lost, either the ligand can wrap around the remaining metal to form a monometallic complex, or two monometallic complexes can dimerize to form double-P4 ligand bimetallic complexes. Neither of the rhodium products shown in Figure 2 is active for hydroformylation. Their structures are based on similar rhodium complexes that have been crystallographically characterized[10,11] and on ^1H and $^{31}P\{^1H\}$ NMR experiments of $[Rh_2(nbd)_2(\textit{rac}\text{-et,ph-P4})]^{2+}$ under H_2/CO pressure.

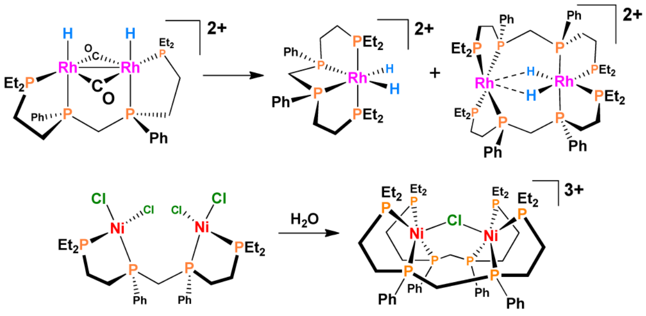


Figure 2. (Top) Two proposed rhodium complexes that are formed from the fragmentation of catalytically active $[Rh_2H_2(\mu\text{-}CO)_2(\textit{rac}\text{-et,ph-P4})]^{2+}$ species during hydroformylation in acetone. (Bottom) $Ni_2Cl_4(\textit{meso}\text{-et,ph-P4})$ that completely converts to the bimetallic double-P4 nickel complex shown when dissolved in a polar organic solvent that contains more than 5% (by volume) water, even at room temperature.[9]

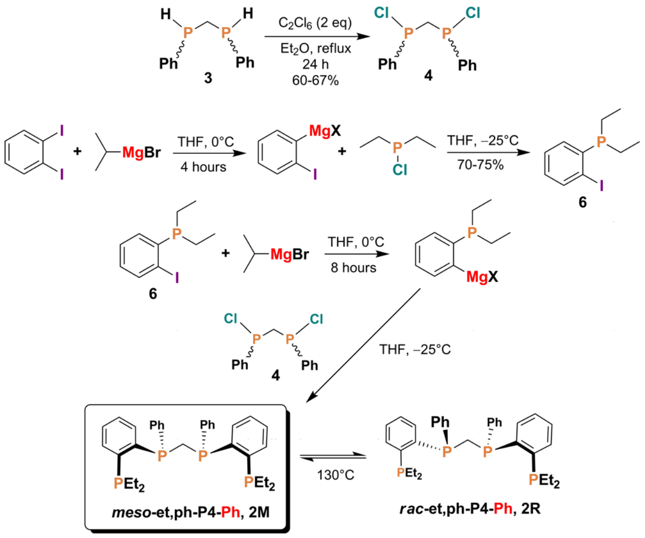
Therefore, the synthesis of a new tetraphosphine ligand in which the rotationally flexible ethylene linkage between the internal and external phosphines is replaced by a rigid phenylene group will lead to a much stronger chelate effect, inhibiting phosphine arm dissociation. This should lead to a more robust dirhodium catalytic system that still has high activity and regioselectivity via bimetallic cooperativity. Herein we report the synthesis and characterization of the new tetraphosphine ligands *rac-* and *meso-*$(Et_2P\text{-}1,2\text{-}C_6H_4)P(Ph)CH_2(Ph)P(1,2\text{-}C_6H_4PEt_2)$ (et,ph-P4-Ph), **2R** and **2M** (Figure 1), and the bimetallic nickel complexes of **2R** and **2M**.

The synthesis of **2R** and **2M** is depicted in Scheme 1. In the first step, $(H)(Ph)PCH_2P(Ph)(H)$ (**3**) is reacted with 2 equiv of hexachloroethane[12] and refluxed in diethyl ether for 24 h to give, after workup, $(Cl)(Ph)PCH_2P(Ph)(Cl)$ (**4**) as a slightly pink air-, moisture-, and heat-sensitive viscous liquid that has been fully characterized (see the Supporting Information, SI).[13,14] The $^{31}P\{^1H\}$ NMR spectrum of **4** shows two singlets at 81.3 and 81.0

Received: August 8, 2014
Published: September 10, 2014

dx.doi.org/10.1021/ic5019345 | *Inorg. Chem.* 2014, 53, 10036−10038

Scheme 1. Synthesis of 2R and 2M



ppm in benzene-d_6 due to *rac* and *meso* diastereomers. However, only one resonance can be observed at high concentrations or in a nonaromatic solvent; e.g., the ^{31}P NMR spectrum of **4** in CD_2Cl_2 shows only one singlet at 82.0 ppm. This is presumably due to intermolecular interactions that result in the accidental degeneracy of the resonances depending on the solvent and/or concentration.

The next stage involves a two-step process to make 1-(Et_2P)-2-iodobenzene (**6**).[15] 1,2-Diiodobenzene is reacted with *i*PrMgBr, then treated with Et_2PCl, and allowed to stir overnight. After workup, **6** is isolated as an air-, moisture-, and light-sensitive colorless liquid in 70−75% yield.[16]

The final step of the synthesis involves another Grignard-mediated P−C coupling reaction. **6** is reacted with *i*PrMgBr followed by the addition of **4** and allowed to stir overnight. An initial workup of this reaction mixture allowed us to isolate a white paste, which was identified as a 1:1 mixture of **2R** and **2M** in 75−81% yield. Part of this initial workup involved short-path vacuum distillation of the crude reaction mixture around 130 °C to remove unreacted **6** and other volatile impurities. However, ^1H NMR experiments monitoring the distinctive central methylene protons of **2R** and **2M** demonstrate that the crude reaction mixture contains mostly (>95%) the *meso* diastereomer. It is only after the crude product is heated that a 1:1 mixture of both diastereomers is obtained. Although **4** exists as an approximately 1:1 mixture of diastereomers, the final P−C coupling forms mainly the *meso* diastereomer for reasons not currently understood. Heating **2M** at 130 °C for only 1−2 h leads to complete epimerization. Thus, if one wants **2M**, only very mild heating should be employed during the solvent removal and ligand isolation steps. Currently, the only way to obtain **2R** is to racemize **2M** and separate the individual diastereomers.

Purification and separation of crude **2M** and **2R** can be achieved directly via column chromatography. The crude mixture of the final epimerized product can be initially purified using a neutral alumina column and eluting with CH_2Cl_2. This removes a large portion of the impurities present in the crude ligand mixture (19−25% impurities). A second longer neutral alumina (grade IV) column using a 1:4 mixture of CH_2Cl_2/hexanes allows for good separation of **2M** and **2R** with only a small interface containing a mixture of both diastereomers, which can be recycled. Additionally, the need for short-path vacuum distillation to remove **6** is eliminated because it usually comes out of the separation column in the first 5 × 10 mL fractions, followed by **2M** and then **2R**. The isolated yield of et,ph-P4-Ph after chromatography is 60−65%.

The $^{31}P\{^1H\}$ NMR of each diastereomer is shown in Figure 3 along with the ^1H NMR of the methylene bridge region, which more clearly identifies the *rac* and *meso* ligand diastereomers. The ^{31}P NMR for each diastereomer is a complex second-order pattern because of the closeness of the chemical shifts and coupling constants between the internal and external phosphorus atoms. The ^1H NMR of the methylene bridge hydrogen atoms is much more useful for identifying the purity of each diastereomer.

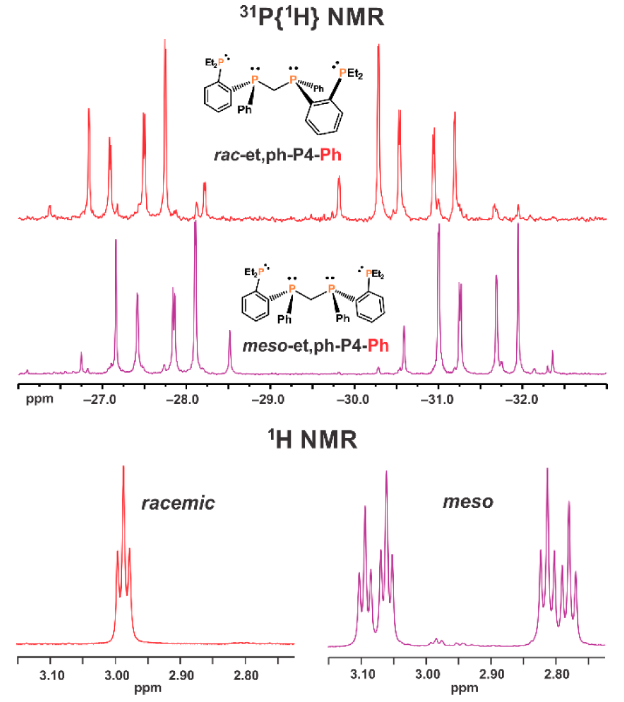


Figure 3. (Top) $^{31}P\{^1H\}$ NMR of *rac*- and *meso*-et,ph-P4-Ph showing the second-order patterns for each diastereomer. (Bottom) ^1H NMR of the methylene bridge region for each diastereomer.

The ligand was reacted with 2 equiv of $NiCl_2 \cdot 6H_2O$ to form the bimetallic nickel complexes in order to more fully characterize the ligand's coordinating ability for making bimetallic complexes. As with **1R** and **1M**, one can use a 1:1 mixture of **2R** and **2M** and the proper solvents to get a fairly clean separation of the two dinickel P4 diastereomers.[2,17] Dissolving the mixed ligand in CH_2Cl_2 and adding this solution to $NiCl_2 \cdot 6H_2O$ in 1-butanol produces an orange powder that precipitates out of solution. After filtration to remove the orange powder, the remaining dark-red solution is allowed to sit overnight, during which small orange crystals precipitate out of solution.

NMR analysis of both the filtered orange powder and orange crystals from the dark-red filtrate revealed them to be the pure *meso* diastereomer, Ni_2Cl_4(*meso*-et,ph-P4-Ph) (**7M**). A workup of the remaining dark-red solution affords an orange powder, which consists of an 87:13 mixture of Ni_2Cl_4(*rac*-et,ph-P4-Ph), **7R**, and **7M**. Both powders can be recrystallized from either acetonitrile or acetone to give crystals suitable for single-crystal X-ray diffraction. The acetone-derived crystals have two molecules of **7M** and acetone per asymmetric unit. ORTEP plots of **7R** and **7M** are shown in Figure 4.

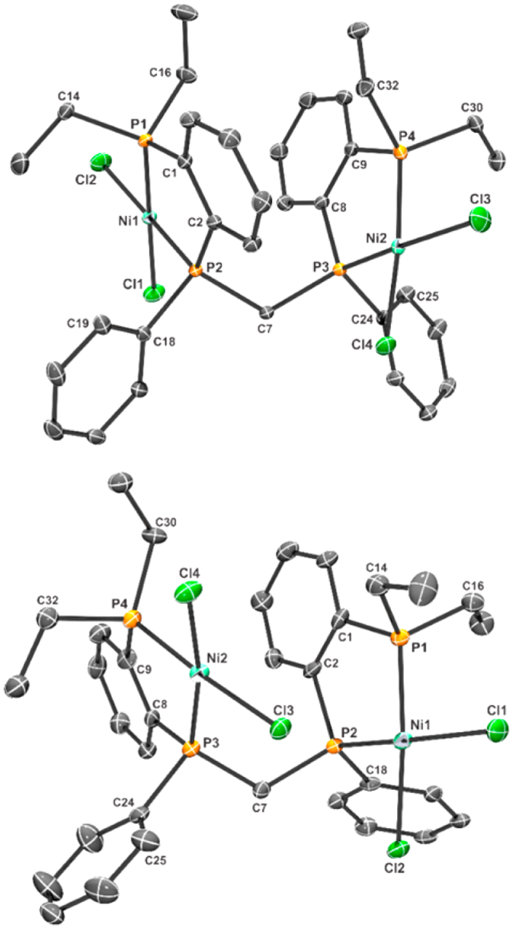


Figure 4. ORTEPs of **7R** (top) and **7M** (bottom; one molecule from the acetone solvate structure). Hydrogen atoms omitted for clarity.

The crystal structures revealed the expected square-planar arrangement of two Cl^- ligands *cis* to each other along with two phosphine moieties chelated through the phenylene linkage for both metal centers. The bond lengths are very similar to those seen for Ni_2Cl_4(**1R**) and Ni_2Cl_4(**1M**)[2] and to one another (see the SI). The biggest difference between **7R** and **7M** is the rotational conformation about the central methylene bridge. For **7R**, the nickel centers are symmetrically rotated away from one another, adopting a completely open-mode geometry in which the nickel centers are on opposite sides of the molecule with a Ni−Ni separation of 5.9031(1) Å and a Ni1−P2···P3−Ni2 torsional angle of 130.14(1)°.

This conformation is similar to the solid-state structure of Ni_2Cl_4(**1R**), which also adopts an open-mode conformation. However, the Ni−Ni separation (5.417 Å) and Ni1−P···P′−Ni2 torsional angle (105.82°) are both smaller for Ni_2Cl_4(**1R**).[2] **7M** adopts a partially closed-mode geometry with a Ni−Ni distance ranging between 4.272 and 4.434 Å and an average Ni1−P2···P3−Ni2 torsional angle of 42.2°. This is facilitated by a weak interaction between Ni1 and Cl3 with an average distance of 3.046 Å. This solid-state conformation is quite different from Ni_2Cl_4(**1M**), which adopts an open-mode structure with a longer Ni−Ni separation (6.272 Å) and a much larger Ni1−P2···P3−Ni2 torsional angle (160°) compared to those of **7M.**[2]

We believe that the far stronger chelate effect of this new P4 ligand will produce catalysts that will have the high activity and regioselectivity observed with the previous ligand **1R** but be far more resistant to deactivating fragmentation reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, spectroscopic data (NMR and IR spectra of P4 ligands; ^{31}P NMR data on Ni_2 complexes), and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gstanley@lsu.edu.

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the NSF (Grant CHE-0111117), Sasol North America, Louisiana Board of Regents (OPT-IN & Graduate Fellowship Program), and a summer graduate student research assistantship from Eastman Chemical are gratefully acknowledged.

■ REFERENCES

(1) Laneman, S. A.; Fronczek, F. R.; Stanley, G. G. *J. Am. Chem. Soc.* **1988**, *110*, 5585−5586.

(2) Laneman, S. A.; Fronczek, F. R.; Stanley, G. G. *Inorg. Chem.* **1989**, *28*, 1872−1878.

(3) Broussard, M. E.; Juma, B.; Train, S. G.; Peng, W.-J.; Laneman, S. A.; Stanley, G. G. *Science* **1993**, *260*, 1784−1788.

(4) Matthews, R. C.; Howell, D. K.; Peng, W.-J.; Train, S. G.; Treleaven, W. D.; Stanley, G. G. *Angew. Chem., Int. Ed.* **1996**, *35*, 2253−2256.

(5) Aubry, D. A.; Bridges, N. N.; Ezell, K.; Stanley, G. G. *J. Am. Chem. Soc.* **2003**, *125*, 11180−11181.

(6) Matthews, R. C. In Situ Spectroscopic Studies of a Bimetallic Hydroformylation Catalyst. Ph.D. Dissertation, Louisiana State University, Baton Rouge, LA, 1999.

(7) Gueorguieva, P. G. Spectroscopic and Synthetic Studies Relating to a Dirhodium Hydroformylation Catalyst. Ph.D. Dissertation, Louisiana State University, Baton Rouge, LA, 2004.

(8) Polakova, D. Studies on a Dirhodium Tetraphosphine Hydroformylation Catalyst. Ph.D. Dissertation, Louisiana State University, Baton Rouge, LA, 2012.

(9) Schreiter, W. J. Investigations into Alkene Hydration and Oxidation Catalysis. Ph.D. Dissertation, Louisiana State University, Baton Rouge, LA, 2013.

(10) Hunt, C., Jr.; Fronczek, F. R.; Billodeaux, D. R.; Stanley, G. G. *Inorg. Chem.* **2001**, *40*, 5192−5198.

(11) Hunt, C., Jr.; Nelson, B. D.; Harmon, E. G.; Fronczek, F. R.; Watkins, S. F.; Billodeaux, D. R.; Stanley, G. G. *Acta Crystallogr., Sect. C* **2000**, *56*, 546−548.

(12) Weferling, N. *Z. Anorg. Allg. Chem.* **1987**, *548*, 55−62.

(13) Gol, F.; Hasselkuß, G.; Knüppel, P. C.; Stelzer, O. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43*, 31−44.

(14) Schmidbaur, H.; Schnatterer, S. *Chem. Ber.* **1986**, *119*, 2832−42.

(15) Boymond, L.; Rottländer, M.; Cahiez, G.; Knochel, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 1701−1703.

(16) Schreiter, W. J.; Monteil, A. R.; Peterson, M. A.; McCandless, G. T.; Fronczek, F. R.; Stanley, G. G. *Polyhedron* **2013**, *58*, 171−178.

(17) Aubry, D. A.; Laneman, S. A.; Fronczek, F. R.; Stanley, G. G. *Inorg. Chem.* **2001**, *40*, 5036−5041.