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A New Class of Binucleating Tetratertiaryphosphine Ligands. The Synthesis and Crystallographic Characterization of the Chiral Diastereomer of a Rhodium(I) Dimer: $Rh_2Cl_2(CO)_2$(eLTTP) (eLTTP = $(Et_2PCH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PEt_2)$)

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The hexatertiaryphosphine ligand $(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2$, eHTP, has proven to be a powerful binucleating ligand system for transition-metal centers, and we have prepared and crystallographically characterized a variety of bimetallic systems based on eHTP.[1-5] Our primary interest is in studying the cooperative behavior between two (or more) metal centers for promoting novel reactions, particularly in homogeneous catalysis. One potential concern with eHTP is that it is a rather sterically encumbering ligand when the metal centers are in proximity to each other. We would now like to report the synthesis of a new binucleating *tetra*tertiaryphosphine ligand based on the eHTP template which is not only considerably less bulky but has two diastereomers, one of which exists in an optically active form. The synthesis and structure of a rhodium(I) dimer based on this tetratertiaryphosphine ligand system is also presented.

Substituting two of the $-CH_2CH_2PR_2$ linkages on eHTP with phenyl groups produces the linear tetratertiaryphosphine ligand $(R_2CH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PR_2)$, LTTP,[6] that is less sterically hindered yet retains the unique combination of bridging and chelating functionalities that make eHTP such a powerful binucleating ligand system. This substitution imposes chiral character on the two central phosphorus atoms and results in two possible sets of diastereomers: the meso *R,S* form and the racemic chiral *R,R* and *S,S* enantiomeric pair. The synthetic procedure used to synthesize LTTP (R = Et, Ph) is shown in Scheme I.[7] The preparation of the key $Ph(H)PCH_2P(H)Ph$ intermediate was previously reported by Stelzer and co-workers.[8]

Table I. Selected Bond Distances (Å) and Angles (deg) for $Rh_2Cl_2(CO)_2$(eLTTP)·THF[a]

Rh–Rh′	5.813 (2)	P1–C′	1.87 (1)
Rh–Cl	2.382 (4)	P1–C(11)	1.86 (1)
Rh–P1	2.289 (4)	P1–C1P	1.84 (2)
Rh–P2	2.229 (5)	P2–C(12)	1.88 (2)
Rh–C(1)	1.87 (2)	O1–C(1)	1.11 (2)
		C(11)–C(12)	1.46 (2)
Cl–Rh–P1	89.7 (1)	C′–P1–C(11)	109.0 (6)
Cl–Rh–P2	173.1 (2)	C′–P1–C1P	100.8 (7)
Cl–Rh–C(1)	93.5 (6)	C11–P1–C1P	103.1 (7)
P1–Rh–P2	83.4 (2)	P1–C′–P1′	113. (1)
P1–Rh–C(1)	176.8 (6)	P1–C(11)–C(12)	105. (1)
P2–Rh–C(1)	93.4 (6)	P2–C(12)–C(11)	113. (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

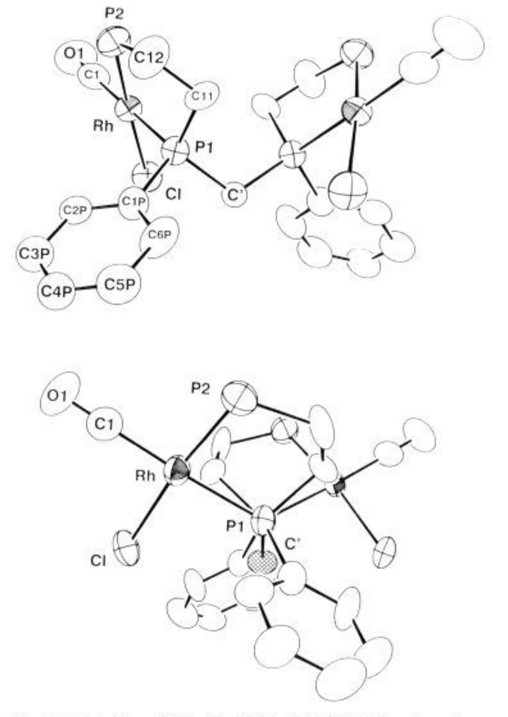
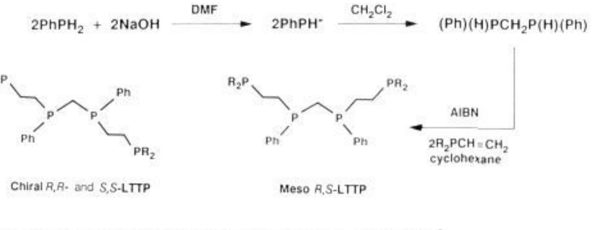


Figure 1. ORTEP plots of $Rh_2Cl_2(CO)_2$(eLTTP) showing views parallel (top) and perpendicular (bottom) to the central P1–P1′ axis. The molecule lies on a crystallographic 2-fold rotation axis that passes through the central methylene bridge (C′) of the eLTTP ligand. The two ethyl groups on P2 are omitted for clarity in both ORTEP plots. The central methylene group carbon atom (C′) has been hatched in the lower perpendicular view to emphasize its position. Thermal ellipsoids are represented at the 33% probability level.

Scheme I



The first linear tetratertiaryphosphine $(Ph_2PCH_2CH_2)(Ph)PCH_2CH_2P(Ph)(CH_2CH_2PPh_2)$, tetraphos, prepared by King and co-workers,[9] had a central ethylene bridge and was designed to trischelate a single metal center, although bimetallic complexes

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[6] We use the LTTP abbreviation to distinguish this more linear ligand from the tripodal tetratertiaryphosphine ligand $P(CH_2CH_2PR_2)_3$ and the tridentate phosphine $PhP(CH_2CH_2CH_2PPh_2)_2$ which is also commonly abbreviated as ttp.

[7] Synthesis of eLTTP: All manipulations were carried out under inert atmosphere conditions with appropriately dried and degassed solvents. $Et_2PCH{=}CH_2$[1] (3.84 g, 0.033 mol), 3.84 g (0.0165 mol) of $PhHPCH_2PHPh$,[8] 50 mL of cyclohexane, and 0.0384 g (0.23 mmol) of AIBN were added to a 100-mL Schlenk flask equipped with a condenser and refluxed overnight. After cooling the solvent was vacuum evaporated, and the flask was equipped with a short-head distillation column. A 0.1 Torr vacuum was established, and the remaining colorless viscous liquid was gradually heated to 170 °C, and the volatile impurities allowed to distill off. The ruckstand contains nearly pure eLTTP (>98%) with an isolated yield of 88%: ^{31}P NMR (CH_2Cl_2, δ, H_3PO_4 ref) diastereotopic internal phosphorus atoms, −26.2 (1 P, t, J_{P-P} = 10.8 Hz) and −25.5 (1 P, t, J_{P-P} = 10.8 Hz); terminal phosphines, −18.3 (2 P, d, J_{P-P} = 9.8 Hz); ^1H NMR (MeOH-d_4, δ) 0.74–0.88 (m, P-CH_2-CH_3), 1.02–1.14 (m, P-CH_2-CH_3), 1.19–1.33, 1.33–1.46 (m, P-CH_2-CH_2-P), 1.72–1.89 (m, P-CH_2-P), 6.98–7.10 and 7.41–7.47 (m, Ph). Synthesis of pLTTP: The synthesis of pLTTP was carried out in an analogous fashion with $Ph_2PCH{=}CH_2$, although the workup and isolation procedure is different. After vacuum evaporation of the cyclohexane from the final reaction mixture, the very viscous clear and colorless liquid is taken up in 20 mL of Et_2O and placed in a −40 °C freezer overnight. A white, powdery precipitate forms on the sides of the flask which is mainly the meso diastereomeric form (ca. 80%). The racemic chiral diastereomer does not easily crystallize. Total isolated yield: 85–90%. Isolated yield of white precipitate (ca. 80% meso), 25–35%: ^{31}P NMR (CH_2Cl_2, δ, H_3PO_4 ref) diastereotopic internal phosphorus atoms, −25.7 (1 P, t, J_{P-P} = 15.7 Hz) and −25.2 (1 P, t, J_{P-P} = 16.4 Hz); terminal phosphines, −11.9 (2 P, t, J_{P-P} = 14.8 Hz); ^1H NMR (MeOH-d_4, δ) 1.82–2.00, 2.01–2.13, 2.14–2.22 (m, P-CH_2-CH_2-P), 2.24 (t, P-CH_2-P), 7.12 and 7.37 (m, Ph). Satisfactory analytical data (C, H) were obtained for both ligands (Oneida Research Services, Whitesboro, NY.).

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were occasionally formed.[10] Stelzer reported the low yield preparation of $(iPr_2PCH_2CH_2CH_2)(iPr)PCH_2P(iPr)(CH_2CH_2CH_2P\text{-}iPr_2)$, but this ligand has *not* been used to prepare any reported transition-metal dimer complexes.[11] We decided to use ethylene-linked terminal phosphines in LTTP because they simplify the synthetic procedure and give higher yields of the final tetratertiaryphosphine (88–92% yield based on $Ph(H)PCH_2P(H)Ph$, 39–43% yield based on starting $PPhH_2$). The use of phenyl rings on the internal phosphines is another designed feature which should facilitate the crystallization of transition-metal dimer complexes for structural analyses. Although the all-phenyl-substituted LTTP ligand was prepared, our primary interest is in the ethyl-substituted LTTP (eLTTP) ligand because the electron rich alkylated terminal phosphines will coordinate strongly to transition-metal centers and be more effective at inhibiting dimer fragmentation processes (vide infra).

The reaction of eLTTP with $Rh_2(\mu\text{-}Cl)_2(CO)_4$ generates the golden-orange rhodium(I) eLTTP dimer $Rh_2Cl_2(CO)_2$(eLTTP), **1**.[12] An X-ray structure[13] on the material that crystallizes out of THF first reveals that the chiral *R,R*- and *S,S*-eLTTP diastereomer is present and has indeed coordinated to two Rh(I) centers. Parallel and perpendicular views of the dimer are shown in the ORTEP diagrams in Figure 1 with selected bond distances and angles listed in Table I. The dimer lies on a 2-fold rotation axis that passes through the central methylene bridge of the eLTTP ligand. The coordination geometry about the metal center is square planar with the expected distortions away from ideal due to the five-membered chelate ring. Surprisingly, not only is this the first reported crystal structure on two $MX(CO)(P_2)$ moieties linked together into a dimer complex, but it is also the first structurally characterized example of a $MX(CO)(P_2)$ (M = Rh, Ir; X = halide; P_2 = five-membered ring chelating bistertiaryphosphine) unit.

The Rh_2(eLTTP) dimer adopts an open-mode conformation in which the two $RhCl(CO)P_2$ halves are symmetrically splayed apart by rotations about the central methylene bridge. The Rh–Rh separation is 5.813 (2) Å with a Rh–P1···P1′–Rh′ torsional angle of 123°. This open-mode orientation is similar to those seen for some eHTP binuclear systems which have symmetrically splayed M1–P···P–M2 torsional angles ranging from 58° to 102°.[3,5] A major difference, however, is that the central $P–CH_2–P$ angle of 113 (1)° for $Rh_2Cl_2(CO)_2$(eLTTP) is markedly smaller than those observed for related $M_2Cl_2(eHTP)^{2+}$ systems which range from 126.6 (4)° for $Pd_2Cl_2(eHTP)^{2+}$ to 129.7 (9)° for $Pt_2Cl_2(eHTP)^{2+}$.[3,14] This unquestionably points to significantly reduced steric interactions between each half of the eLTTP ligand system and strongly suggests that rotations about the central methylene bridge should be facile and could allow the metal centers to interact or cooperate in the activation or reaction of a substrate.

The difference between the stabilities of **1** and the somewhat related dimer $Rh_2(\eta^4\text{-}COD)_2$(tetraphos) is demonstrated by the fact that the tetraphos-based Rh(I) dimer reacts with H_2 under *ambient* conditions to *readily* fragment to the mononuclear species $Rh(\eta^4\text{-tetraphos})^+$.[10e] $Rh_2Cl_2(CO)_2$(eLTTP), in marked contrast, shows no signs of fragmentation even under considerably more rigorous conditions (50 bar H_2/CO, 80 °C). The catalytic activity of mononuclear $MX(CO)P_2$ (M = Rh, Ir) species is well studied, and it will be most interesting to see if the metal centers in this unique eLTTP bridged dimer system can cooperate to produce novel reactivities.

Acknowledgment. We thank the National Science Foundation (CHE-8613089) for supporting this research.

Supplementary Material Available: Tables of crystal and structure refinement parameters, positional parameters, anisotropic thermal parameters, and full bond distances and angles (4 pages); a listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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[12] eLTTP (0.235 g, 0.51 mmol) in 25 mL of THF is gradually added via a cannula to 0.197 g (0.51 mmol) of $Rh_2(\mu\text{-}Cl)_2(CO)_4$ in 25 mL of THF in a dry ice/acetone bath under inert atmosphere conditions. The yellow Rh solution turns a golden-red color after the first drop of eLTTP, and the solution was occasionally flushed with N_2 to remove any CO released from the reaction which was allowed to gradually warm to room temperature and left to stir overnight. A small amount (0.06 g) of an unidentified red-brown precipitate was separated by filtration, and the red-orange filtrate vacuum evaporated to dryness. The orange-red solid was redissolved in ca. 20 mL of THF which deposited small X-ray quality orange-red crystals of a uniform morphology of the racemic chiral-eLTTP diastereomer upon slow evaporation of solvent. Total isolated yield of $Rh_2Cl_2(CO)_2$(eLTTP), 40–47%; isolated crystalline yield of *chiral*-$Rh_2Cl_2(CO)_2$(eLTTP), 15–20%. Spectroscopic data on the structurally characterized *chiral*-$Rh_2Cl_2(CO)_2$(eLTTP): IR (KBr, ν_{CO}) 1970 cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, ppm, H_3PO_4 reference) 77.65 (dd, 1 P, external phosphorus atom, $J_{P-P} = 31.3$ Hz, $J_{Rh-P} = 148.9$ Hz), 48.65 (m, 1 P, internal phosphorus atom, $J_{Rh-P} = 139.3$ Hz). Satisfactory analytical data (C, H) was obtained on toluene recrystallized samples of **1** (Oneida Research Services, Whitesboro, NY.).

[13] Crystallizes in the monoclinic space group *P*2/*c* with the following unit cell parameters: $a = 13.419$ (3) Å, $b = 9.361$ (2) Å, $c = 15.574$ (6) Å, $\beta = 102.62$ (3)°, $V = 1909$ (1) Å^3, $Z = 2$. Data were collected on an Enraf-Nonias CAD4 diffractometer with Mo Kα radiation, and an empirical absorption correction was performed. The structure was refined by using the Enraf-Nonius SDP program set to give final discrepancy indices of $R = 0.048$ and $R_w = 0.062$ with a GOF = 1.15 based on 989 unique data with $F_o^2 > 3\sigma(F_o^2)$. The terminal ethyl groups on the eLTTP ligand were disordered and successfully modeled and refined with isotropic thermal parameters; a disordered THF solvent molecule lying on the 2-fold axis could not, however, be modeled, and an unusually large anisotropic thermal parameter for the THF oxygen atom resulted. The data set was limited due to the small size of the crystal and its less than ideal diffraction characteristics. Tables of X-ray data collection and structure solving parameters, positional parameters, anisotropic thermal parameters, full bond distances and angles, and observed and calculated structure factors are included in the Supplementary Material.

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An "Expanded Porphyrin": The Synthesis and Structure of a New Aromatic Pentadentate Ligand

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The porphyrins and related tetrapyrrole macrocycles are among the most versatile of *tetradentate* ligands.[1] Attempts to stabilize higher coordination geometries, however, with larger porphyrin-like aromatic macrocycles have met with little success.[2-5] Indeed, to date, only the uranyl complex of "superphthalocyanine" has

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[1] *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978-1979; Vols. I-VII.

[2] "Superphthalocyanine", a pentaaza aromatic phthalocyanine-like system was prepared by a uranyl-mediated condensation; it is not obtainable as the free-base or in other metal-containing forms: (a) Day, V. W.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1975**, *97*, 4519-4527. (b) Marks, T. J.; Stojakovic, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 1695-1705. (c) Cuellar, E. A.; Marks, T. J. *Inorg. Chem.* **1981**, *208*, 3766-3770.

[3] Bauer, V. J.; Clive, D. R.; Dolphin, D.; Paine, J. B. III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S.-W. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6429–6436. To date only tetracoordinated metal complexes have been prepared from these potentially pentadentate ligands.

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[5] Mertes et al. have recently characterized a five-coordinate copper complex of an elegant (but nonaromatic) porphyrin-like "accordion" ligand derived from dipyrromethines: (a) Acholla, F. V.; Mertes, K. B. *Tetrahedron Lett.* **1984**, 3269–3270. (b) Acholla, F. V.; Takusagawa, F.; Mertes, K. B. *J. Am. Chem. Soc.* **1985**, 6902–6908. Four-coordinate copper complexes of other *nonaromatic* pyrrole-containing macrocycles have also been prepared recently: Adams, H.; Bailey, N. A.; Fenton, D. A.; Moss, S.; Rodriguez de Barbarin, C. O.; Jones, G. *J. Chem. Soc., Dalton Trans.* **1986**, 693–699.

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