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Design, Synthesis, and Chemistry of Sterically Nondemanding Primary Bisphosphines[1]

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Abstract: Design and synthesis of chelating bisphosphines functionalized with the smallest chemical unit "H" on the P^{III} centers ($(PH_2CH_2)_2CHCH_2NHPh$ (**4**) and $(PH_2CH_2)_2CHCONHPh$ (**5**)) are described. Studies demonstrating that no bulky chemical substituents are necessary to offer thermal/oxidative stability to the $-PH_2$ groups in **4** and **5** are described. The H atoms around the P^{III} centers in **5** (or **4**) concur limited/no steric influence, but yet the phosphines manifest high nucleophilicity to coordinate strongly with W(0) and Re(I). The studies include synthesis and X-ray structural characterization of an air-stable primary bisphosphine (**5**) and its transition-metal chemistry with $W(CO)_6$ and $Re(CO)_5Br$ to produce the complexes (η^2-$(PH_2CH_2)_2CHCONHPh)W(CO)_4$ (**6**) and (η^2-$(PH_2CH_2)_2CHCONHPh)Re(CO)_3Br$ (**7**), respectively.

Introduction

Transition-metal compounds derived from functionalized phosphine ligands have attained ubiquitous prominence in homogeneous catalysis.[2−4] The spatial disposition of substituents around the P^{III} center plays a pivotal role in providing such important properties as chirality and geometrical/steric constraints. Indeed, systematic variations of substituents on P^{III} centers is an effective tool for tuning of electronic effects in phosphine ligands and in their corresponding transition-metal complexes. The chemical architecture of substituents defines the cone angle around the P^{III} center, and such properties play important roles in the catalytic activity of coordinated metal complexes.[5−7] Therefore, functionalization and fine-tuning of substituents around P^{III} centers is an activity of continued interest in the overall design and development of phosphine ligands for transition-metal-based homogeneous catalysts.[8−11] A vast majority of studies toward functionalized monophosphine or chelating bisphosphine ligands have involved functionalization with alkyl, aryl, alkoxy, aryloxy, or chiral functionalities. Despite extensive transition-metal chemistry and catalytic investigations on a plethora of functionalized bisphosphines, the corresponding studies of the primary bisphosphines (e.g., H_2PXPH_2, X = alkyl or aryl) has remained largely unexplored.[12,13] This may be in part be due to difficulties associated with the synthesis and oxidative/thermal instability of functionalized primary bisphosphines.[14] Design and development of "user-friendly" [15] primary bisphosphines and their coordination chemistry with transition-metal precursors would be of paramount importance because the hydrogen substituents on the P^{III} centers provide "minimal" sterical hindrance. Indeed, our knowledge base on the transition-metal/organometallic chemistry of chelating phosphine ligands with less bulky substituents and their consequent influence in catalytic transformations is yet limited. In this context, the development of primary bisphosphines that exhibit optimum oxidative/thermal stability will aid in their utility as chelating

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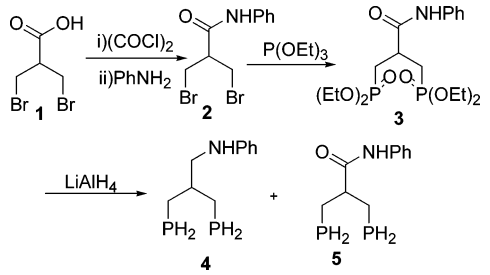
Scheme 1. Synthesis of **4** and **5**



agents and consequently expand our understanding of the nature of their interaction with transition metals.

As part of our ongoing studies[12,13,16−20] on the main-group and transition-metal chemistry of functionalized phosphines, we herein report the synthesis, characterization, and X-ray crystal structure of an air-stable primary bisphosphine, *N*-phenyl-3-phosphanyl-2-(phosphanylmethyl)propionamide (**5**). In an effort to elucidate the σ versus the π bonding capabilities of **5**, in this paper we also report the reaction chemistry of **5** with $W(CO)_6$ and $Re(CO)_5Br$ compounds, including the X-ray crystal structures of (η^2-$(PH_2CH_2)_2CHCONHPh)W(CO)_4$ (**6**) and (η^2-$(PH_2CH_2)_2CHCONHPh)Re(CO)_3Br$ (**7**).

Results and Discussion

Our rationale for the chemical architecture of primary bisphosphines included two motives: (a) that the primary bisphosphine framework display optimum oxidative stability to perform transition-metal chemistry studies; and (b) that the transition-metal centers "strictly" interact with the two P^{III} primary phosphine centers with no interference from any ancillary coordinating units within the ligand backbone. The second criterion stems from our overall objective of trying to understand the coordinating chemistries of the primary phosphine within chelating environments.

The air-stable primary bisphosphine $(PH_2CH_2)_2CHCONHPh$ (**5**) was synthesized via synthetic routes as shown in Scheme 1. The dibromo acid **1** was converted to its corresponding acid chloride by treatment with oxalyl chloride, which upon treatment with aniline produced the corresponding amide **2**. The dibromo amide **2** was converted to the bisphosphonate **3** by refluxing in triethyl phosphite. The reduction of **3** always resulted in two products, aminobisphosphine **4** and amidobisphosphine **5**, despite varying the reaction conditions. The yield of amide **5** was increased to 18% upon reduction of **3** at 0 °C in diethyl ether followed by quenching the reaction mixture after 15 min. ^{31}P NMR spectroscopic analysis of the reaction products indicated the presence of the unreacted phosphonate **3**. Higher yields of the amine **4**, with concomitant consumption of **3**, were isolated upon increasing the duration of this reaction. These two products (**4** and **5**) were separated using silica gel column chromatography. Compound **4** is a liquid, whereas compound **5** is an air-stable crystalline solid at room temperature. The new

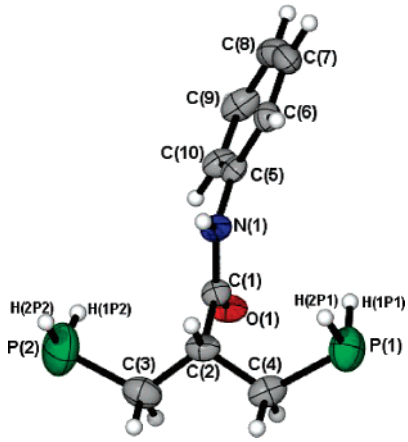


Figure 1. ORTEP diagram of **5**.

primary bisphosphines **4** and **5** were characterized by NMR spectroscopy (^1H, ^{31}P, and ^{13}C) and mass spectrometry. Compound **5**, which exhibits remarkable air stability, has been characterized by elemental analysis. The high-field signals at −149.6 and −142.9 ppm for **4** and **5**, respectively, were attributed to the primary phosphine moiety.[21] The amide group (in **5**) versus the amine group (in **4**) exerted minimal influence on the $^1J_{P-H}$ values ($^1J_{P-H}$ in **5**, 197.0 Hz; $^1J_{P-H}$ in **4**, 196.7 Hz).

The amine- and amide-functionalized primary phosphine analogues **4** and **5** are remarkably stable in air and in organic solvents (THF, CH_2Cl_2, toluene, etc.). In fact, no detectable oxidation was noted upon storing crystalline **5** for over 12 months in glass vials. It is important to recognize that the alkyl- and aromatic-functionalized primary bisphosphines $H_2P-X-PH_2$ (X = alkyl or aryl) are so unstable that they instantaneously ignite upon exposure to air. Recent studies have demonstrated that bulky groups around the P^{III} centers render oxidative inertness to primary phosphines.[22−28] Examples of primary phosphines with sterically demanding substituents include compounds with triptcyl, 2,4,6-tri-*tert*-butylphenyl, anthracyl, and dibenzobarllenyl groups on the P(III) center.[22−28] The unusual oxidative stability demonstrated by the primary bisphosphine **5** is particularly significant as it provides a rare example of achieving oxidative inertness without the size-dominating effects of a bulky functional group. To address if any intermolecular interactions influence the high oxidative stability of the primary phosphine units in **5**, we have undertaken an X-ray crystal structure investigation of this compound.

Crystals suitable for single-crystal X-ray diffraction studies of **5** were obtained from a dichloromethane solution of **5**. The

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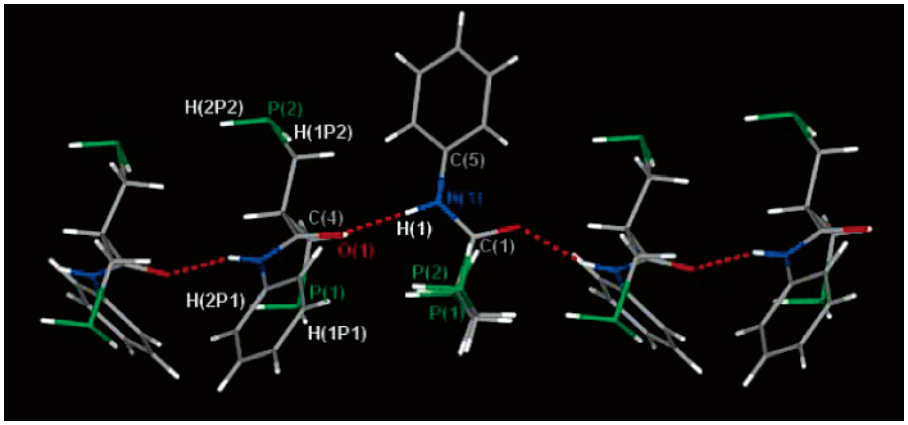
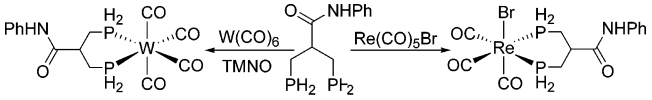


Figure 2. H-bonding in **5**.

Scheme 2. Interactions of **5** with $W(CO)_6$ or $Re(CO)_5Br$



6 **5** **7**

primary phosphine **5** crystallized in the rhombohedral crystal system with a molecule of the solvent of crystallization. The ORTEP plot of **5**, as shown in Figure 1, confirms the molecular constitution of the primary bisphosphine. The structure reveals P−C bond lengths in **5** (1.839(4) and 1.835(4) Å) comparable to those observed in primary phosphines, (ferrocenylmethyl)phosphine (1.850(3) Å), and dibenzobarallenylphosphine (1.859(4) Å)), which are functionalized with sterically demanding ancillary substituents.[22−28] The structure of **5** further consisted of intermolecular hydrogen-bonding interactions between the amide (N−H) and carbonyl (C═O) groups of the adjacent molecule, producing an infinite linear chain as shown in Figure 2. It may be noted that there were no direct hydrogen bonds with the hydrogens of the primary phosphine centers. Therefore, the oxidative inertness of **5** as a consequence of any hydrogen-bonding interactions with the $-PH_2$ may be discounted.

Almost all of the reported crystal structures of free primary monophosphines contain a bulky group attached to the phosphorus, to sterically crowd the phosphorus atom and thereby render stability to P−H bonds.[22−28] In this context, the amide-functionalized primary bisphosphine **5** is a rare example of its kind demonstrating excellent oxidative stability in the absence of any bulky substituent. The reason for the unusual oxidative stability of primary bisphosphine **5** is unclear. However, observations from our earlier work[18,20] and also as noted by Stelzer and co-workers[25] suggest that electronegative heteroatoms such as nitrogen or sulfur, two or three carbons away from the phosphorus, may have negative hyperconjugative electronic influence on the P(III) centers and thus render the primary phosphine oxidatively stable.[18,20]

Interaction of 5 with Transition Metals. The user-friendly properties of the primary bisphosphine **5** provided an important rationale to explore the reactivity of "sterically nondemanding" "PH_2" groups in **5** toward organometallic precursors $W(CO)_6$ and $Re(CO)_5Br$. The complexation reactions of **5** with metal carbonyls are shown in Scheme 2. Primary bisphosphine **5** reacts with tungsten hexacarbonyl in the presence of decarbonylating agent trimethylamine *N*-oxide to produce the *cis*-[$W(CO)_4\{\eta^2$-$PH_2CH_2CH(CONHPh)CH_2PH_2\}$] (**6**) complex. The bisphosphine **5** reacts with $Re(CO)_5Br$ in acetonitrile under refluxing conditions to yield two products, with resonances at $\delta = -108.5$ (major) and $\delta = 115.2$ (minor) ppm, as indicated by the ^{31}P NMR spectrum of the crude reaction mixture. Only one product, *fac*-[$Re(CO)_3\{\eta^2$-$PH_2CH_2CH(CONHPh)CH_2PH_2\}Br$] (**7**), was isolable upon column chromatographic purification. Complexes **6** and **7** have been characterized by ^{31}P and ^1H NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction.

The $^{31}P\{^1H\}$ NMR spectrum of **6** showed a singlet at $\delta = -111.0$ ppm with tungsten satellites ($^1J_{P-W} = 206.0$ Hz). The proton-coupled ^{31}P NMR spectrum of **6** showed a triplet, with $^1J_{P-H}$ coupling of 328.0 Hz, indicating that the bisphosphine binds to the metal center without deprotonation of the PH_2 centers. Similarly, the $^{31}P\{^1H\}$ NMR spectrum of **7** showed a singlet at $\delta = -108.5$ ppm, and the proton-coupled spectrum showed a triplet with $^1J_{P-H}$ coupling of 355.9 Hz. The ^{31}P NMR resonances of **6** and **7** shifted downfield with respect to the parent primary phosphine ligand.[23,29−31]

The molecular structures of **6** and **7** were determined by single-crystal X-ray diffraction analysis. Single crystals of **6** were obtained from dichloromethane/ethanol solution, and the crystals of **7** were obtained from slow evaporation of ethyl acetate solution. The tungsten (**6**) and rhenium (**7**) complexes of **5** crystallized in the orthorhombic crystal system (Table 1). The ORTEP plots for **6** and **7** are depicted in Figures 3 and 4, respectively. Important bond lengths and bond angles for **5**−**7** are listed in Table 2, and a complete list of bond distances and angles are included in the Supporting Information. The crystal structures of **6** and **7** establish the *cis*-η^2 coordination of ligand **5**. The tungsten and rhenium atoms in complexes **6** and **7** exhibit distorted octahedral geometry. The P−M−P bond angles in **6** and **7** are 85.49(6)° and 85.86(5)°, respectively. A closer examination of the crystal packing diagram and intermolecular distances in compounds **6** and **7** reveals no intermolecular

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Table 1. Crystallographic Data for **5**−**7**

	5	6	7
empirical formula	$C_{10.17}H_{11}Cl_{0.25}NOP_2$	$C_{14}H_{15}NO_5P_2W$	$C_{13}H_{15}BrNO_4P_2Re$
fw	234.03	523.06	577.31
cryst size (mm)	0.4 × 0.15 × 0.10	0.40 × 0.20 × 0.02	0.40 × 0.30 × 0.15
cryst syst, space group	rhombohedral, R_3	orthorhombic, *Pbca*	orthorhombic, $P2_12_12_1$
a (Å)	21.5254 (13)	8.6521(8)	6.5297 (4)
b (Å)	21.5254 (13)	17.2931(15)	13.6202(9)
c (Å)	14.1730(12)	23.187(2)	19.8064(13)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	120	90	90
V (Å^3)	5687.2 (7)	3469.3(5)	1761.5(2)
Z	18	8	4
λ (Å)	0.71073	0.71073	0.71073
D_c (Mg/m^3)	1.230	2.003	2.177
T (K)	173(2)	173(2)	173(2)
R^a (obsd data)			
R1	0.0628	0.0453	0.0273
wR2	0.1682	0.0898	0.0651

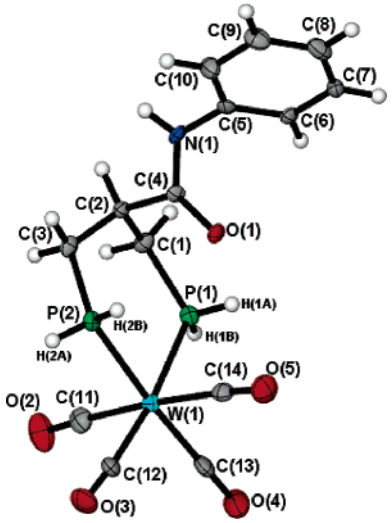

Figure 3. ORTEP diagram of **6**.

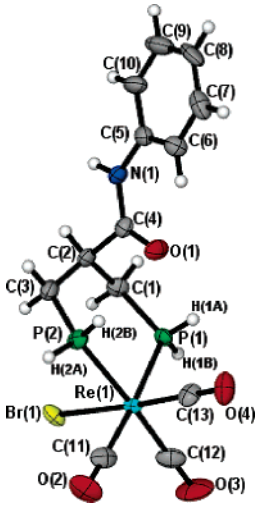

Figure 4. ORTEP diagram of **7**.

hydrogen bonding between primary phosphine hydrogens and C═O or N−H groups.

Stereochemical and Electronic Implications. The crystallographic data for the W(0) and Re(I) metallacycles suggests that the six-membered rings in **6** and **7** are nonplanar. The metallacycles adopt an energetically (thermodynamically) favored chair conformation, similar to the favorable conformation observed in cyclohexane and its derivatives. It is striking to note that **6** and **7** adopt a chair conformation despite the fact that P−M−P bond angles in these complexes are 85.49(6)° and 85.85(5)°, respectively. Indeed, these angles represent a significant deviation from the regular bond angle (111.5°) found in cyclohexane.

The average metalphosphine bond lengths in **6** and **7** (W−P = 2.487 Å and Re−P = 2.4339 Å) are strikingly similar to those observed for the W(0)/Re(I) complexes derived from alkyl- or aryl-substituted phosphines.[22−28] This finding suggests that *σ* donation, being the dominant electronic contribution in complexes derived from the primary phosphines (e.g., **6** and **7**), may indeed account for the sole electronic factor providing kinetic stability. This unique electronic effect complemented

Table 2. Bond Lengths (Å) and Bond Angles (deg) for **5**−**7**

atoms	distance	atoms	angle
	Compound **5**		
P1−C4	1.839(4)	P1−C4−C2	118.3(2)
P2−C3	1.835(4)	P2−C3−C2	117.0(2)
C2−C4	1.535(5)	C4−C2−C3	110.2(3)
C2−C3	1.532(5)	C2−C1−O1	121.2(3)
C1−O1	1.230(3)	C2−C1−N1	115.7(2)
C1−N1	1.353(4)		
	Compound **6**		
W1−P1	2.502(2)	P1−W2−P2	85.49(6)
W1−P2	2.472(2)	P1−W1−C12	173.2(2)
W1−C11	2.024(9)	P2−W1−C13	175.4(2)
W1−C12	1.988(8)	C11−W1−C14	176.1(3)
W1−C13	1.985(9)	C12−W1−C13	92.9(3)
W1−C14	2.018(8)	W1−C11−O2	177.1(8)
P1−C1	1.842(7)	C1−C2−C3	113.5(6)
P2−C3	1.833(7)	C2−C4−O1	121.7(6)
C4−O1	1.242(8)		
	Compound **7**		
Re1−P1	2.4346(16)	P1−Re1−P2	85.86(5)
Re1−P2	2.4332(16)	P1−Re1−C12	92.58(19)
Re1−Br1	2.6434(6)	P2−Re1−C11	90.64(19)
Re1−C11	1.938(7)	C13−Re1−Br1	176.9(2)
Re1−C12	1.929(7)	C11−Re1−C12	90.7(3)
Re1−C13	1.910(6)	Re1−C11−O2	178.8(6)
P1−C1	1.825(6)	C1−C2−C3	115.5(5)
P2−C3	1.836(6)	C2−C4−O1	120.7(5)
C4−O1	1.219(7)		

by the chemical architecture of the smallest substituents in the primary bisphosphine framework **5** and its metal complexes **6** and **7** may be of paramount importance in catalytic applications. The small size of "H" substituents in **6** and **7** is expected to facilitate easy access of substrate molecules around metal centers. The juxtaposition of minimum steric hindrance may provide high degrees of freedom and proximity, particularly for the sterically demanding substrates.

Conclusions

Hydrogen substituents of the P^{III} centers in **5** and in the corresponding W(0) and Re(I) metal complexes **6** and **7**, respectively, exert important electronic influence on the coordinating metals. The presence of H substituents on the P^{III} centers in **5** decreases their π-back-bonding capabilities. This electronic effect concomitantly increases the electron densities of the primary-phosphine-bound metals. It is well-known that an increase in the electron density of metals will lead to efficient oxidative addition processes across the metal-catalyzed organic transformations.[4] Therefore, transition-metal/organometallic compounds derived from chelating primary bisphosphines will play important roles in catalytic processes.

Experimental Section

All reactions were carried out under nitrogen by standard Schlenk techniques. All chemicals were obtained from Aldrich Chemical Co. and were used without further purification. NMR spectra were recorded on a Bruker ARX-300 spectrometer using the specified solvent. ^{1}H and ^{13}C chemical shifts are reported in parts per million, downfield from internal standard $SiMe_4$. ^{31}P NMR (121.5 MHz) spectra were recorded with 85% H_3PO_4 as an external standard and positive chemical shifts downfield of the standard. Mass spectra were recorded at Washington University, St. Louis, MO, and combustion analysis was done by Oneida Research Services, Whitesboro, NY.

Crystallographic Data Collection and Refinement of Structure. A suitable crystal was chosen and mounted on a glass fiber with epoxy resin. The crystal data and refinement results were given in Table 1. See the Supporting Information for CIF files. Data reduction and processing followed routine procedures. Structures were solved by direct methods and refined on F_o^2. Absorption corrections were done by semiempirical equivalents.

Synthesis of $(BrCH_2)_2CHCONHPh$ (2). To a vigorously stirring, cold (0 °C) solution of 3-bromo-2-(bromomethyl)propionic acid (**1**) (10.0 g, 40.6 mmol) in benzene (100 mL) was slowly added oxalyl chloride (6.0 mL, 69.7 mmol), followed by dimethylformamide (0.2 mL). The reaction mixture was stirred at room temperature for 14 h, and solvent was removed under vacuum to afford the corresponding acid chloride (10.6 g, 40.0 mmol). The acid chloride was dissolved in anhydrous CH_2Cl_2 (40 mL) and added to an ice cold stirring solution of aniline (8.1 g, 88.0 mmol) in CH_2Cl_2 (100 mL) over a period of 20 min, and the resulting mixture was stirred for 14 h. The reaction mixture was diluted with CH_2Cl_2 (600 mL) and washed with 2 N HCl (2 × 75 mL), followed by brine (100 mL), and then with saturated $NaHCO_3$ (2 × 75 mL). The organic layer was further washed with brine (2 × 100 mL) and dried with anhydrous sodium sulfate. Removal of solvent under reduced pressure gave the crude amide product **2**. Compound **2** was purified on a silica gel column (ethyl acetate/hexane, 4%) to give 12.1 g of **2** (91% yield) in 98% purity. HRMS (*m*/*z*): $(M^+ + H)$ for $C_{10}H_{11}Br_2NO$, calcd 319.9286, obsd 319.9295. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.53 (d, 2H, J = 7.80 Hz), 7.35 (t, 2H, J = 8.10 Hz), 7.16 (t, 1H, 7.20 Hz), 3.73−3.67 (m, 2H), 3.60−3.55 (m, 2H), 3.12−3.09 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 168.5, 137.1, 129.3, 125.4, 120.7, 53.2, 31.1.

Synthesis of $((EtO)_2P(O)CH_2)_2CHCONHPh$ (3). Amide **2** (12.1 g, 38.0 mmol) was refluxed for 16 h in excess triethyl phosphite, which also served as the solvent. Volatile products were distilled off at reduced pressure to afford the crude product as a yellow viscous oil. The crude product upon purification on a silica gel column (ethyl acetate/hexane, 30%) yielded 13.91 g (85% yield) pure bisphosphonate **3**. HRMS (ionized with LiCl) (*m*/*z*): for $C_{18}H_{31}NO_7P_2Li$, calcd 442.1736, obsd 442.1746. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 9.17 (br s, 1H), 7.59 (d, 2H, J = 8.40 Hz), 7.35−7.25 (m, 2H), 7.07 (t, 1H, J = 7.20 Hz), 4.14−3.98 (m, 8H), 3.21−3.05 (m, 1H), 2.38−2.07 (m, 4H), 1.31−1.18 (m, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 170.6 (t, $^3J_{P-C}$ = 7.5 Hz), 138.3, 128.8, 123.9, 119.5, 62.1−61.9 (m), 36.2, 28.9 (dd, $^1J_{P-C}$ = 140.7 Hz, $^3J_{P-C}$ = 13.1 Hz), 16.3−16.2 (m). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, δ): 30.4.

Synthesis of $(PH_2CH_2)_2CHCH_2NHPh$ (4) and $(PH_2CH_2)_2CHCONHPh$ (5). To a cold (0 °C) solution of **3** (1.39 g, 32.0 mmol) in diethyl ether (250 mL) was added dropwise a 1 M solution of $LiAlH_4$ in ether (80 mL), and stirring was continued for 20 min. The excess LAH was quenched by wet ether, and the ethereal layer was washed with 2 N HCl (2 × 75 mL) followed by brine (2 × 100 mL). The organic layer was separated and dried with anhydrous sodium sulfate to yield a mixture of **4** and **5**, which were separated on a silica gel column (ethyl acetate/hexane, 15%) to yield amine **4** (40% isolated yield) (R_f = 0.5) and amide **5** (18% isolated yield) (R_f = 0.17). The following are data for **4**. HRMS (*m*/*z*): $(M^+ + H)$ calcd 213.0836, obsd 213.0832. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.25−7.16 (m, 2H), 6.76−6.68 (m, 1H), 6.65 (br d, 2H, J = 8.62 Hz), 3.2 (d, 2H, J = 6.5 Hz), 2.72 (dt, 4H, $^1J_{P-H}$ = 196.7 Hz, $^1J_{H-H}$ = 7.3 Hz), 2.05−1.88 (m, 1H), 1.85−1.7 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 148.0, 129.4, 117.5, 112.8, 47.8, 40.7, 16. ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, δ): −149.6. The following are data for **5**. Anal. Calcd for $C_{10}H_{15}NOP_2$: C, 52.87; H, 6.66; N, 6.17. Found: C, 53.13; H, 6.51; N, 5.98. HRMS (*m*/*z*): $(M^+ + H)$ calcd 228.0707, obsd 228.0712. IR (KBr pellet, cm^{-1}): ν_{P-H} 2298 (sh, s), ν_{CO} 1657 (sh, s). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.52 (d, 2H, J = 8.10 Hz), 7.32 (t, 2H, J = 7.80 Hz), 7.12 (t, 1H, J = 7.20 Hz), 3.08−3.00 (m, 2H), 2.39−2.29 (m, 3H), 2.20−1.97 (m, 2H), 1.82−1.76 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 171.9, 137.2, 129.0, 124.7, 120.3, 53.5, 18.2 (d, $^1J_{P-C}$ = 12.1 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, δ): −142.9.

Synthesis of $W(CO)_4\{\eta^2\text{-}(H_2PCH_2)_2CHCONHC_6H_5\}$ (6). To a slurry of $W(CO)_6$ (200 mg, 0.56 mmol) in CH_3CN (5 mL) was added dropwise a solution of trimethylamine *N*-oxide (132.9 mg, 1.12 mmol) in CH_3CN (15 mL). The resulting yellow-colored solution was stirred for 20 min. To this solution was slowly added compound **5** (127 mg, 0.56 mmol) in CH_3CN (10 mL), and the resulting solution was refluxed for 4 h, followed by removal of solvent under reduced pressure to give crude product **6** as a pasty mass. The crude compound was purified on a silica gel column (methanol/dichloromethane, 2%) to give 176 mg (60% yield) of pure product **6** (isolated yield 60%). ^{1}H NMR ($CDCl_3$/DMSO, 300 MHz, δ): 7.37(br d, 2H, J = 8.1 Hz), 7.12 (br t, 2H, J = 8.1 Hz), 6.90 (br t, 1H, J = 7.42 Hz), 4.60 (md, 4H, $^1J_{P-H}$ = 328 Hz) 2.84 (m, 1H), 2.32 (m, 2H), 1.98 (m, 2H). ^{13}C NMR (CD_2Cl_2, 75 MHz, δ): 171.2, 137.6, 129.4, 125.2, 120.3, 44.2, 19.0 (t, J_{C-P} = 16.6 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz, δ): −111 (s, $^1J_{P-W}$ = 206 Hz). EI-MS (*m*/*z*): [M^+] for $(CO)_4WP_2$, calcd 523, obsd 523. IR (KBr pellet, cm^{-1}): ν_{CO} 1866 (br s), 2018 (sh, s), ν_{PH} 2336 (sh, w). Anal. Calcd for $C_{14}H_{15}NO_5P_2W$: C, 32.15; H, 2.89; N, 2.68. Found: C, 32.69; H, 2.96; N, 2.51.

Synthesis of $ReBr(CO)_3\{\eta^2\text{-}(H_2PCH_2)_2CHCONHC_6H_5\}$ (7). A solution of **5** (60 mg, 0.26 mmol) and rhenium pentacarbonyl bromide (107 mg, 0.26 mmol) in anhydrous acetonitrile (10 mL) was refluxed for 17 h. The solvent was removed to obtain the crude product. The crude product was purified on a silica gel column (50% ethyl acetate, hexane) to yield 83 mg (55% yield) of pure product **8** (isolated yield 52%). ^{1}H NMR (CD_3CN, 300 MHz, δ): 7.53−7.58 (m, 2H), 7.32−7.39 (m, 2H), 7.14 (m, 1H), 5.42−5.50 (m, 1H), 5.12−5.20 (m, 1H),

4.15−4.26 (m, 1H), 3.94−4.09 (m, 1H), 3.45−3.71 (m, 1H), 2.38−2.59 (m, 2H) 2.31−2.37 (m, 2H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz, δ): −108.50. IR (KBr pellet, cm^{-1}) ν_{CO} 1903 (sh, s), 1953 (sh, s), 2033 (sh,s), ν_{PH} 2415 (s, w). Anal. Calcd for $C_{13}H_{15}BrNO_4P_2Re$: C, 27.05; H, 2.62; N, 2.43. Found: C, 28.20; H, 2.53; N, 2.08.

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Supporting Information Available: Crystallographic data of **5**−**7** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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