Double C−H Activation Results in Ruthenium Complexes of a Neutral PCP Ligand with a Central Carbene Moiety

Wei Weng,[†] Sean Parkin,[‡] and Oleg V. Ozerov*[,†]

Departments of Chemistry, Brandeis University, MS 015, 415 South Street, Waltham, Massachusetts 02454, and University of Kentucky, Lexington, Kentucky 40506

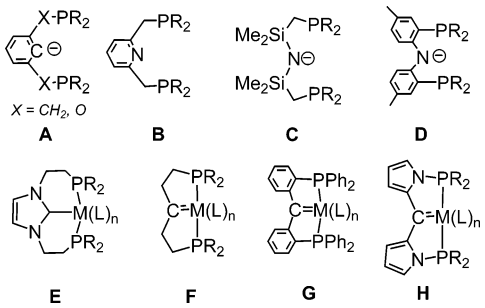
Received May 26, 2006

Ru complexes of a new neutral PCP pincer ligand containing a central carbene ligand have been prepared (referred to as (P_2C═) for emphasis). The ligand precursor P_2CH_2 can be prepared in good yield in two steps from pyrrole, formaldehyde, and chlorodiisopropylphosphine. The reaction between P_2CH_2 and [(*p*-cymene)$RuCl_2$]$_2$ in the presence of Et_3N cleanly furnishes (P_2C═)RuHCl. The latter possesses a Y-shaped five-coordinate geometry about Ru, as determined in an X-ray diffraction study. Reactions of (P_2C═)RuHCl with a series of potential ligands have been examined. Addition of pyridine, MeCN, or ethylene leads to a simple adduct formation and addition of CO leads to coordination of two CO ligands to Ru with concomitant hydride-to-carbene migration, while addition of PMe_3 gives rise to both types of products. (P_2C═)RuHCl is a moderately active precatalyst for transfer hydrogenation of ketones. Addition of phenylacetylene leads to the insertion of the triple bond into Ru−H to give (P_2C═)Ru(−CPh═CH_2)-Cl. (P_2C═)RuHCl can be converted to (P_2C═)$RuCl_2$ by action of an iminium chloride reagent. (P_2C═)$RuCl_2$ adds one molecule of CO with retention of the carbene moiety, even at elevated temperatures. These results demonstrate the potential of (P_2C═) as a robust and electronically distinctive ancillary ligand.

Introduction

Pincer ligands incorporating two phosphine arms and a central donor site Z have attracted a substantial amount of interest since the initial investigations of PCP ligands by Shaw.[1] Several variations of the central donor atom Z have been explored. Ligands with Z = aryl (**A**, Chart 1) remain the most widely used.[2] Such monoanionic PCP ligands have been found to support a number of exciting catalytic and stoichiometric transformations.[3,4] Isoelectronic neutral PNP ligands carrying a neutral pyridine donor as the Z group (**B**) have also been used.[5] Ligands with Z = amido were first introduced by Fryzuk (**C**) and have since been employed by others.[6,7] More recently, several groups, including ours, have been focusing on PNP ligands with a central diarylamido motif (**D**).[8−13]

Chart 1



The above three types of Z moieties are either primarily a σ donor (aryl, pyridine) or a $\sigma + \pi$ donor (amido). We were interested in designing a PZP pincer ligand where the central Z

* To whom correspondence should be addressed. E-mail: ozerov@brandeis.edu.

[†] Brandeis University.

[‡] University of Kentucky.

(1) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

(2) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759.

(3) (a) Gottker-Schnetmann, I.; White, P.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804. (b) Krogh-Jespersen, K.; Czerw, M.; Zhu, K.; Singh, B.; Kanzelberger, M.; Darji, N.; Achord, P. D.; Renkema, K. B.; Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 10797. (c) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086. (d) Haenel, M. W.; Oevers, S.; Angermund, K.; Kaska, W. C.; Fan, H.-J.; Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3596−3600.

(4) (a) Morales-Morales, D.; Redon, R.; Yung, C.; Jensen, C. M. *Chem. Commun.* **2000**, 1619. (b) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379. (c) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687.

(5) (a) Nelson, S. M.; Dahlhoff, W. V. *J. Chem. Soc. A* **1971**, 2184. (b) Giannoccaro, P.; Vasapollo, G.; Sacco, A. *J. Chem. Soc., Chem. Commun.* **1980**, 1136. (c) Hahn, C.; Spiegler, M.; Herdtweck, E.; Taube, R. *Eur. J. Inorg. Chem.* **1999**, 435. (d) Liu, S. H.; Lo, S. T.; Wen, T. B.; Zhou, Z. Y.; Lau, C. P.; Jia, G. *Organometallics* **2001**, *20*, 667. (e) Hahn, C.; Morvillo, P.; Herdtweck, E.; Vitagliano, A. *Organometallics* **2002**, *21*, 1807. (f) Ben-Ari, E.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 4714. (g) Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Milstein, D. *Organometallics* **2004**, *23*, 4026. (h) Cucciolito, M. E.; D'Amora, A.; Vitagliano, A. *Organometallics* **2005**, *24*, 3359. (i) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2005**, *127*, 10840.

(6) (a) Fryzuk, M. D. *Can. J. Chem.* **1992**, *70*, 2839. (b) Fryzuk, M. D.; Berg, D. J.; Haddad, T. S. *Coord. Chem. Rev.* **1990**, *90*, 137. (c) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1.

(7) (a) Ozerov, O. V.; Huffman, J. C.; Watson, L. A.; Caulton, K. G. *J. Am. Chem. Soc.* **2004**, *126*, 6363. (b) Watson, L. A.; Ozerov, O.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2003**, *125*, 8426. (c) Watson, L. A.; Coalter, J. N., III; Ozerov, O.; Pink, M.; Huffman, J. C.; Caulton, K. G. *New J. Chem.* **2003**, 263.

(8) Liang, L.-C. *Coord. Chem. Rev.* **2006**, *250*, 1152.

(9) (a) Liang, L.-C.; Chien, P.-S.; Lin, J.-M.; Huang, M.-H.; Huang, Y.-L.; Liao, J.-H. *Organometallics* **2006**, *25*, 1399. (b) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007.

(10) Winter, A. M.; Eichele, K.; Mack, H.-G.; Potuznik, S.; Mayer, H. A.; Kaska, W. C. *J. Organomet. Chem.* **2003**, *682*, 149.

(11) Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 2030.

(12) (a) Bailey, B. C.; Fan, H.; Baum, E. W.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 16016. (b) Bailey, B. C.; Huffman, J. C.; Mindiola, D. J.; Weng, W.; Ozerov, O. V. *Organometallics* **2005**, *24*, 1390.

10.1021/om060464r CCC: $33.50
Publication on Web 09/28/2006

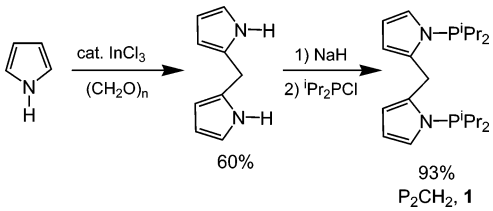
moiety is a π-acceptor. The diarylamido PNP system can be viewed as a chelating analogue of the ubiquitous *mer*-$Cl(R_3P)_2$ substructure. Part of our motivation in investigating a π acceptor as Z in PZP is to fashion a chelating analogue of the similarly common *mer*-$(CO)(R_3P)_2$ motif. A central carbene moiety as Z would serve well in this regard. The two prior examples of PZP pincer-type ligands where Z = carbene are found in complexes **E**[14] and **F**[15a] (Chart 1). Lee's ligand in **E** incorporates an N-heterocyclic carbene. Carbenes of this sort are generally regarded as primarily σ donors and at best only weak π acceptors (compared to non-heteroatom-substituted carbenes).[16] Gusev's example **F** contains an unambiguous π-acceptor carbene; however, in this ligand, carbene/olefin isomerization is a distinct possibility (the olefin isomer is, in fact, preferred for Ru).[15a,b] In addition, the backbone of bis(phosphine)pentane is quite flexible and in certain cases is unable to enforce coordination of both phosphine arms to the same metal center.[15b]

In our pursuit of a design that would contain a π-acceptor carbene that is immune to isomerization and is rigid enough to enforce unremitting tridentate coordination, we were guided by our explorations of PNP ligands. In the PNP case, linking the phosphine arms and the central amido donor with *o*-arylene tethers eliminated several undesirable problems associated with other PNP designs. Inspired in part by the Gusev example, we envisioned that the carbene moiety might be accessed (with an appropriate metal) via double CH activation of the central CH_2 group in a ligand precursor. We first considered a design based on the bis(*o*-phosphinophenyl)methane structure (**G**), in direct analogy to bis(*o*-phosphinophenyl)amine (**D**). Roper et al. reported Ru complexes of **G**; however, in that case the ligand was formed serendipitously within the metal coordination sphere from two PPh_3 units and a Ru−CF_3 group and such an approach is not at all generally applicable.[17] Because of the considerations of synthetic feasibility, we turned our attention instead to the closely related system **H**. Here we take advantage of the synthetically trivial N−P bond construction while keeping the benefits of a rigid 1,2-arylene linker between the outer and inner pincer donor atoms. In this report we present the synthesis of this new ligand and its viability as a precursor for the (P_2C═)Ru complexes. We will use the (P_2C═) notation to differentiate the new ligand from aryl-based PCP ligands and to emphasize its carbene central unit.

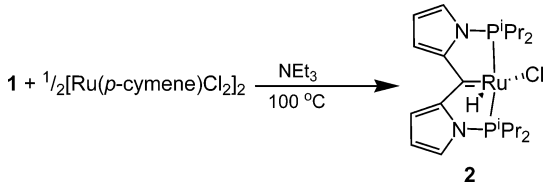
Results

Preparation of Ligand. Dipyrromethane was prepared from the Lewis acid catalyzed condensation reaction between paraformaldehyde and excess pyrrole developed by Lindsey et al.[18]

Scheme 1



Scheme 2



Deprotonation of dipyrromethane with excess NaH in THF and subsequent addition of 2 equiv of $^iPr_2PCl$ afforded the product P_2CH_2 (**1**; 95%, ^{31}P NMR evidence) (Scheme 1). Compound **1** was isolated as a pale yellow oil in 93% yield upon workup and was successfully used in the next stage without further purification. **1** was characterized by ^1H, ^{13}C, and ^{31}P NMR in solution; it displayed time-averaged C_{2v} symmetry at 22 °C. One singlet resonance (δ 56.8 ppm) in the $^{31}P\{^1H\}$ NMR spectrum, one methine resonance, and two methyl resonances arising from isopropyl groups in the ^1H NMR spectrum were observed. The protons of the CH_2 linkage resonate at δ 4.59 ppm as a singlet in the ^1H NMR spectrum, and the carbon of the CH_2 linkage resonates at δ 27.2 ppm as a triplet with J_{C-P} = 19 Hz in the $^{13}C\{^1H\}$ NMR spectrum.

Synthesis of (P_2C═)Ru(H)(Cl) (2). Thermolysis (Scheme 2) of the mixture of **1**, [Ru(*p*-cymene)$Cl_2]_2$, and triethylamine (100 °C, 12 h) in toluene resulted in a dark red solution with concurrent formation of a white precipitate (presumably Et_3-NHCl). This synthesis follows the preparation of **F** by Gusev et al.[15] ^{31}P NMR analysis in situ suggested clean formation of the Ru hydrido carbene (P_2C═)Ru(H)(Cl) (**2**; >95% yield by NMR). **2** was isolated as an analytically pure reddish solid in 75% yield upon workup. NMR spectra of **2** show characteristic resonances of the hydride at δ −15.3 ppm (^1H NMR, t, J_{H-P} = 18 Hz) and of the carbene carbon at δ 253.0 ppm ($^{13}C\{^1H\}$ NMR, t, J_{C-P} = 8 Hz). **2** displays C_s symmetry in solution on the NMR time scale, exhibiting four different methyl and two methine resonances for the isopropyl groups in its ^1H NMR spectrum and one singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum. The proposed structure was confirmed by an X-ray diffraction study (vide infra).

Reactions of 2 with CH_3CN and Pyridine. Compound **2** is a 16-electron complex that should be endowed with an ability to react rapidly with external substrates. We sought to investigate its reactivity with a range of different ligands. We were particularly interested in whether the *mer*-(P_2C═) coordination is maintained and whether the carbene ligand is merely a spectator moiety.

In C_6D_6 at ambient temperature, **2** reacted with 3 equiv of CH_3CN or pyridine upon mixing to form the 18-electron adduct (P_2C═)RuHCl(L) (**3**, **4**; Scheme 3). Upon cooling of a CD_2Cl_2 solution of (P_2C═)RuHCl($NCCH_3$) to −65 °C, two isomers were detected. We propose that the two isomers are **3a** and **3b**[19] (ca. 3:1 ratio; Ru−H at δ −10.6 ppm (t, J = 20 Hz, major) and

(13) (a) Gatard, S.; Çelenligil-Çetin, R.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2006**, *128*, 2808. (b) Weng, W.; Guo, C.; Çelenligil-Çetin, R.; Foxman, B. M.; Ozerov, O. V. *Chem. Commun.* **2006**, 197. (c) Fan. L.; Parkin, S.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 16772. (d) Fan, L.; Ozerov, O. V. *Chem. Commun.* **2005**, 4450. (e) Weng, W.; Guo, C.; Moura, C. P.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2005**, *24*, 3487. (f) Weng, W.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4700. (g) Fan, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 326.

(14) Lee, H. M.; Zeng, J. Y.; Hu, C.-H.; Lee, M.-T. *Inorg. Chem.* **2004**, *43*, 6822.

(15) (a) Gusev, D. G.; Lough, A. J. *Organometallics* **2002**, *21*, 2601. (b) Gusev, D. G.; Lough, A. J. *Organometallics* **2002**, *21*, 5091.

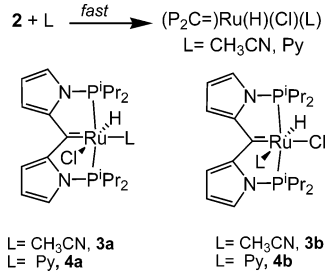
(16) (a) Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407. (b) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239.

(17) Boyd, L. M.; Clark, G. R.; Roper, W. R. *J. Organomet. Chem.* **1990**, *397*, 209.

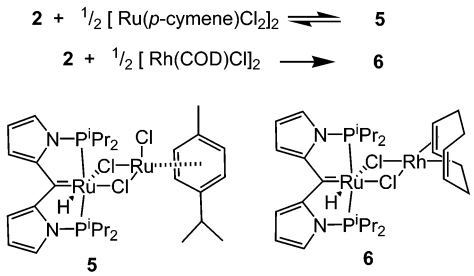
(18) Laha, J. K.; Dhanalekshmi, S.; Taniguchi, M.; Ambroise, A.; Lindsey, J. S. *Org. Process Res. Dev.* **2003**, *7*, 799.

(19) We are unable to assign each of the two sets of resonances observed at −65 °C specifically to **3a** and **3b**.

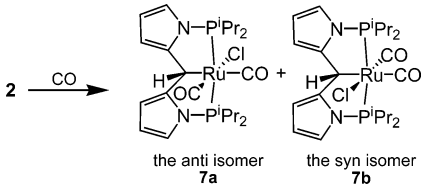
Scheme 3



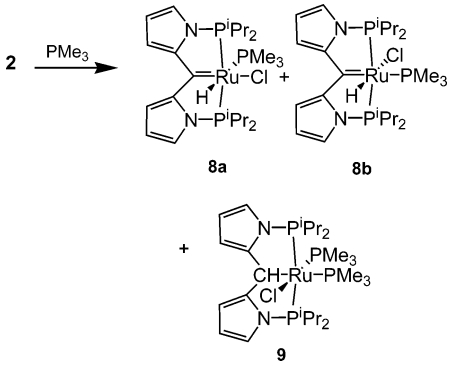
Scheme 4



Scheme 5



Scheme 6



δ −9.2 ppm (t, J = 21 Hz, minor)). On the other hand, only one set of NMR resonances was observed for **3** above −5 °C (Ru−H at δ −10.5 ppm), consistent with a fast exchange between isomers at higher temperature. In concordance with this, only one "average" signal for free and coordinated MeCN was observed by ^{1}H NMR for **3** in the presence of excess MeCN at ambient temperature. Similarly, the ^{1}H NMR spectrum of **4** in C_6D_6 at 22 °C contained only one set of resonances, including that of Ru−H (δ −9.25, t, J = 21.6 Hz). At −60 °C, however, two hydride signals in a 11:1 ratio were observed. An NOE experiment at ambient temperature established no correlation between Ru−H and the ortho CH of coordinated pyridine. This is consistent with a rapidly exchanging mixture of isomers of **4** that is dominated by **4b**. For both **3** and **4**, the carbene functionality and meridional geometry of the (P_2C═) ligand are preserved, as evidenced by the observation of the characteristic ^{13}C NMR resonances of Ru═C and of the virtual coupling for several ^{1}H and ^{13}C NMR resonances, respectively.

Formation of Bimetallic Complexes. Monomeric forms of [Ru(*p*-cymene)Cl_2]$_2$ and [Rh(COD)Cl]$_2$ can be considered κ^1-Cl ligands. The reaction of **2** and [Ru(*p*-cymene)Cl_2]$_2$ in C_6D_6 afforded a mixture of **5** along with **2** and [Ru(*p*-cymene)Cl_2]$_2$ (presumably in equilibrium), while the reaction between **2** and [Rh(COD)Cl]$_2$ resulted in complete conversion to **6** (Scheme 4). Characteristic signals in the ^{1}H NMR spectra (δ −10.6 ppm, t, J_{H-P} = 21.2 Hz, Ru−H) and the ^{13}C{^{1}H} NMR spectra of **6** (δ 253.6 ppm, t, J_{C-P} = 9.1 Hz, Ru═C) provide support for the notion that the hydride neither is bridging nor migrates to the carbene carbon atom but remains bound to the Ru center (no Rh−H coupling was observed).

Reaction of 2 with CO. The reaction of **2** with CO in toluene occurred in the time of mixing with concomitant change of the color of the solution to deep green. In contrast to the formation of simple adducts with CH_3CN or pyridine, the reaction with CO led to the coordination of *two* CO molecules to the Ru(II) center and induced *hydride migration* to the carbene carbon. A mixture of two isomers of **7** (ca. 92:8 ratio) (Scheme 5) was generated upon exposure of a solution of **2** to CO. The spectroscopic features of the major isomer include (1) the absence of a hydride resonance signal in the ^{1}H NMR spectrum, (2) a resonance at δ 5.08 ppm in the ^{1}H NMR spectrum and δ 25.2 ppm in the ^{13}C{^{1}H} NMR spectrum attributable to Ru−CH, (3) resonances at δ 199.2 and 194.5 ppm in the ^{13}C{^{1}H} NMR spectrum for two nonequivalent carbonyl groups, and (4) two IR bands at 2028 and 1954 cm^{-1}. We propose that the two isomers are **7a** and **7b**, differing in the C−H bond of RuCH being either anti to Ru−Cl (**7a**) or syn (**7b**). Crystallization (vide infra) yielded an X-ray-quality crystal of the anti isomer **7a**. It is tempting to assign this to the major observed isomer; however, this cannot be ascertained at this time.

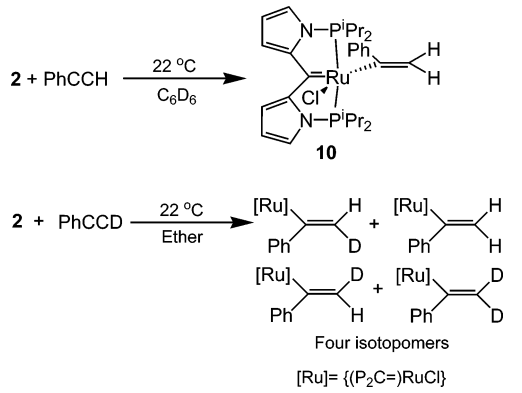
Another plausible isomer for this formulation is one with two CO ligands trans to each other. We tentatively disfavor this isomer on the basis of the near-identical ($\Delta\delta$ = 0.1 ppm) ^{31}P NMR chemical shifts for the observed two isomers. The putative trans isomer would be quite different electronically, and one might have expected to see this difference reflected in the magnitude of the ^{31}P NMR chemical shift difference. The difference between **7a** and **7b**, on the other hand, is marginal. In addition, the intensities of the two CO stretching bands observed by IR spectroscopy for the major isomer (minor isomer bands are obscured) are similar, consistent with the cis and not the trans CO pair.

Reaction of 2 with PMe_3. Addition of PMe_3 (1.2 equiv) to a C_6D_6 solution of **2** resulted in a mixture of **8a**, **8b**, and **9** in a 1:3:2 ratio (Scheme 6). In all compounds, the methyl resonances of ^{i}Pr were realized as doublets of virtual triplets, consistent with a trans disposition of the P^{i}Pr$_2$ arms.[20] The identification of **9** was based on the characteristic Ru−CH resonance at δ 5.80 ppm in the ^{1}H NMR spectrum (as well as the absence of a Ru−H resonance) and an ABX_2 spin system in the ^{31}P NMR spectrum. Reaction of **2** with a larger excess (5 equiv) of PMe_3 resulted in the increased (97%) fraction of **9**. Only one isomer of **9** (in contrast to the analogous CO adducts **7**) was observed by NMR. The structure with trans PMe_3 ligands for **9** can be ruled out on the basis of the small magnitude of J_{PP} corresponding to the coupling between these two ^{31}P nuclei, consistent with their cis disposition. The assignment of **9** as either syn or anti (cf. **7a**/**7b**) cannot be made at this point.

The hydride in **8a** showed a more upfield chemical shift and a larger J_{H-PMe_3} coupling constant than that in **8b** in the ^{1}H NMR spectrum (**8a**, δ −3.96 ppm, dt, J_{H-PMe_3} = 104.3 Hz,

(20) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley-Interscience: New York, 2001; pp 260−262.

Scheme 7



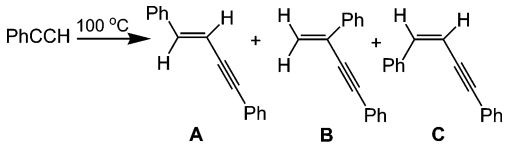
$J_{H-iPPr2} = 27.0$ Hz; **8b**, δ −12.6 ppm, dt, $J_{H-PMe_3} = 29.3$ Hz, $J_{H-iPPr_2} = 18.3$ Hz). The characteristic carbene carbon resonated at δ 253.4 (m) for **8a** and δ 245.4 (dt, $J_{C-PMe_3} = 69.2$ Hz, $J_{C-PiPr_2} = 11$ Hz) for **8b** in the $^{13}C\{^1H\}$ NMR spectrum. **8a** showed larger $PMe_3-P^iPr_2$ coupling (ca. 30 Hz) than **8b** (ca. 13 Hz) in the ^{31}P NMR spectrum. These data are fully consistent with the proposed structural assignment of **8a** (PMe_3 trans to H) and **8b** (PMe_3 trans to carbene).

Reaction of 2 with Phenylacetylene. Treatment of **2** with PhC≡CH at 22 °C in C_6D_6 produced the insertion product $(P_2C=)Ru(-CPh=CH_2)(Cl)$ (**10**) in the time of mixing (Scheme 7). The geminal stereochemistry at the C=C bond of **10** is strongly supported by the observation of the resonances arising from the CH_2 protons as two singlets at δ 5.48 and 4.23 ppm in the ^1H NMR spectrum and also by the solid-state X-ray structural determination (vide infra). The exclusive formation of **10** without *E* or *Z* isomers is somewhat unexpected, since **10** is not the sterically favored isomer.

The reaction of **2** with PhC≡CD afforded a mixture that gave rise to four singlets observed at δ 5.48, 5.47, 4.23, and 4.22 ppm (roughly equal intensity) in the ^1H NMR spectrum and two broad singlets observed at 5.45 and 4.21 ppm (roughly equal intensity) in the ^2H NMR spectrum. We interpret this via formation of four isotopomers (in roughly equal amounts), as shown in Scheme 7, that give rise to *two isotopomeric resonances* for each CH (or CD) position. The larger line width in the ^2H NMR spectrum presumably precludes observation of the requisite *four* signals. We deemed this worthy of special attention because, in and of itself, insertion of PhC≡CD into Ru−H should lead to only one isotopomer of **10**. Exposure of a pure sample of all-protio **10** to PhC≡CD for 2 days at 22 °C did not result in incorporation of D into **10**. This rules out the reversibility of the phenylacetylene insertion (at least in the sense that free phenylacetylene is not released) as the reason for the H/D scrambling. It therefore seems most likely that the H/D scrambling occurs prior to the insertion step via a kinetically more facile but thermodynamically less favorable process (for instance, oxidative addition of the alkynyl CH to Ru in **2**). Similar fast H/D scrambling was observed by Eisenstein, Caulton, et al. in the reactions of terminal alkynes with $(R_3P)_2$-OsHCl(CO).[21] In that study, an unsaturated alkenyl−Os complex was the ultimate product (albeit preferentially yielding a *trans*-alkenyl rather than *gem*-alkenyl isomer), paralleling our report.

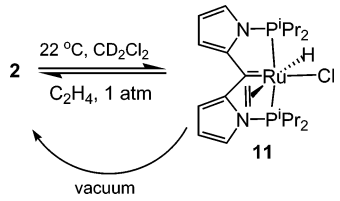
We tested **2** as a precursor for catalytic dimerization of PhC≡CH. Preliminary results are as follows: a mixture of PhC≡CH, **2**, and PhC≡CLi in a 100:1:1 ratio afforded only 30% total conversion to three isomers of enynes A, B, and C after 20 h at 100 °C. The previously reported $(^TPNP)RhH_2$ system showed much higher reactivity and selectivity (Scheme 8).[13b]

Scheme 8



a) 1% **2** and 1% PhCCLi; **A**:**B**:**C**= 18:32:50,32% conversion, 20h.
b) 0.5% $(^TPNP)RhH_2$; **A**:**B**= 99:1,98% conversion, 8h

Scheme 9



Reaction of 2 with Ethylene. The ^1H NMR spectrum of **11** under an ethylene atmosphere (Scheme 9) at 22 °C showed a single broad resonance (δ −7.30 ppm, $\Delta\nu_{1/2} = 627$ Hz) in the hydride region, a broad resonance in the vicinity of the chemical shift of free ethylene, and a complementary set of resonances of the $P_2C=$ ligand. When this solution was cooled below −35 °C, the broad hydride signal decoalesced (coalescence temperature is ca. −5 °C) and gave rise to two well-resolved triplet resonances at δ −3.84 ppm (**11**) and −15.72 ppm (**2**) at −71 °C. Exposure of this solution to vacuum leads to loss of coordinated ethylene and quantitative regeneration of **2**, consistent with weak equilibrium binding of ethylene to **2** in solution. At −71 °C, the protons of the coordinated C_2H_4 gave rise to a slightly broadened singlet (δ 3.13 ppm) in the ^1H NMR spectrum. Any fixed conformation would lead to some nonequivalency among these hydrogens. Ostensibly, the rotation about the $Ru-C_2H_4$ axis is fast (on the NMR time scale), even at −71 °C.[22] We saw no evidence for the formation of an *observable* ethyl insertion product.[23]

Unlike in the case of **3** or **8**/**9**, we observed only one isomer of **11**. We tentatively propose that ethylene is trans to the hydride in the approximately octahedral **11**. The chemical shift of the hydride resonance is most sensitive to what is trans to it. Coordination of a soft donor (such as PMe_3 or C_2H_4) trans to it should engender a farther upfield shift with respect to **2** than would coordination of a hard donor (CH_3CN or Cl). The chemical shift of the hydride in **11** (δ −3.84 ppm) is very close to that in **8a** (δ −3.96 ppm, H trans to PMe_3) and very different from that in **8b** (δ −12.6 ppm, H trans to Cl and cis to PMe_3).

Preparation of $(P_2C=)RuCl_2$ and its Reactivity. The compound $(P_2C=)RuCl_2$ (**12**) was prepared from the reaction of **2** with an equimolar amount of $[Et_2N=CH_2]^+Cl^-$ in moderate yield (60%). Abstraction of hydride from Ru−H by iminium cations was recently studied in detail by Norton et al.[24] An NMR reaction of **12** with excess Ph_2Mg afforded **13** (Scheme 10). The carbene carbon resonates at δ 255.1 ppm (t, $J_{C-P} = 8$ Hz) for **12** and δ 238.2 ppm (t, $J_{C-P} = 9$ Hz) for **13**. Both **12** and

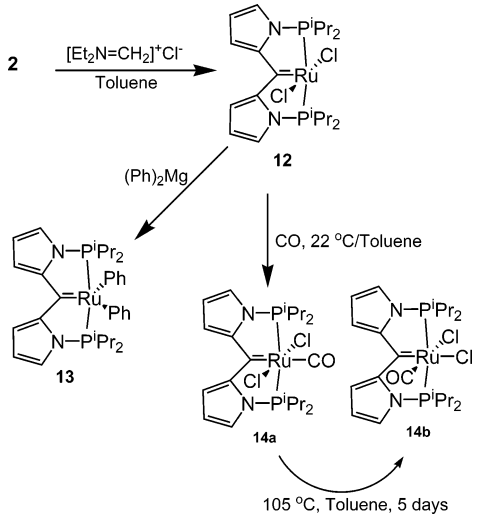
(21) Marchenko, A. V.; Gerard, H.; Eisenstein, O.; Caulton, K. G. *New J. Chem*. **2001**, *25*, 1244.

(22) Friedman, L. A.; Meiere, S. H.; Brooks, B. C.; Harman, W. D. *Organometallics* **2001**, *20*, 1699.

(23) Yi, Chae S.; Lee, Do W. *Organometallics* **1999**, *18*, 5152.

(24) (a) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Janak, K. E. *Organometallics* **2003**, *22*, 4084. (b) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Zhu, G. *J. Am. Chem. Soc*. **2005**, *127*, 7805.

Scheme 10



13 give rise to a C_{2v}-symmetric ^{1}H NMR spectrum at 22 °C (exhibiting two different methyl resonances and only one methine resonance for the isopropyl groups in the ^{1}H NMR spectra). This is consistent with a C_{2v}-symmetric geometry about Ru typical for the Grubbs-type carbenes,[25] of which **12** is a chelating analogue.

The reaction of CO with **12** at 22 °C rapidly afforded **14a** as the only observed product. Slow conversion of **14a** to **14b** was observed at 105 °C in toluene (17 h, 33% conversion; 120 h, 92%). **14b** displays C_s symmetry in solution (exhibiting four different methyl and two methine resonances for the isopropyl groups in the ^{1}H NMR spectra), while **14a** displays C_{2v} symmetry. Characteristic signals in the ^{13}C{^{1}H} NMR spectra for **14a** and **14b** (**14a**, δ 256.1 ppm, t, J = 8 Hz, Ru=*C* and δ 203.1 ppm, t, J = 8.4 Hz, Ru−*C*O; **14b**, δ 239.9 ppm, t, J = 8 Hz, Ru=*C* and δ 200.9 ppm, t, J = 13 Hz, Ru−*C*O) are in agreement with the carbonyl Ru carbene configuration. A single CO-stretching band was observed by IR spectroscopy for both **14a** and **14b**.

X-ray Crystal Structure Analyses. Three Ru complexes (**2**, **7a/7b**, and **10**) have been characterized by single-crystal X-ray diffraction (Figures 1−3). For **2** there are three crystallographically independent molecules per asymmetric unit. Ru−carbene carbon bond distances (ca. 1.91−1.93 Å for Ru−C5 in **2**) are only slightly longer than that in $RuHCl(P^iPr_3)_2[=CN(H)C_3H_6]$ (1.898(6) Å)[26b] but considerably longer than in the Grubbs compound $[RuCl_2(=CHC_6H_4Cl\text{-}p)(PCy_3)_2]$ (1.839(3) Å).[25b] Although the hydrides were not located, the molecular geometry of **2** is probably Y-shaped five-coordinate on the basis of the C5−Ru−Cl bond angle (146.6(2), 150.6(4), and 154.5(3)° for the three molecules, respectively). The environment about Ru in the X-ray crystal structure of **10** is also of the Y-shaped type (the C24−Ru1−Cl1 and C6−Ru1−Cl1 angles are greater than 120°, and the C6−Ru1−C24 angle is less than 90°) and is very similar to that in **2**. Structural preferences of five-coordinate d^6 complexes have been extensively analyzed elsewhere.[26] The C31−Ru1 distance is ca. 3.08 Å, indicating that there is no interaction between the C=C bond and the Ru center. The C31−C24 bond distance in the alkenyl ligand is 1.322(6) Å, a typical C=C bond length.

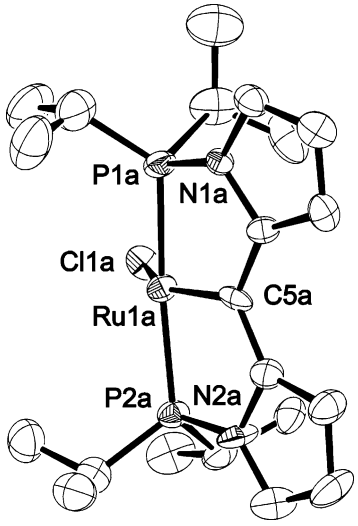


Figure 1. Thermal ellipsoid (50% probability) drawing of **2** (only one molecule is shown here).[27] All H atoms were omitted for clarity. Selected bond distances (Å) and angles (deg) for one of the three nonequivalent molecules: Ru1A−C5A, 1.918(10); Ru1A−P1A, 2.282(2); Ru1A−P2A, 2.300(2); Ru1A−Cl1A, 2.416(2); C5A−Ru1A−P1A, 84.3(3); C5A−Ru1A−P2A, 84.7(3); P1A−Ru1A−P2A, 168.33(10); C5A−Ru1A−Cl1A, 146.6(2); P1A−Ru1A−Cl1A, 93.78(10); P2A−Ru1A−Cl1A, 97.59(9).

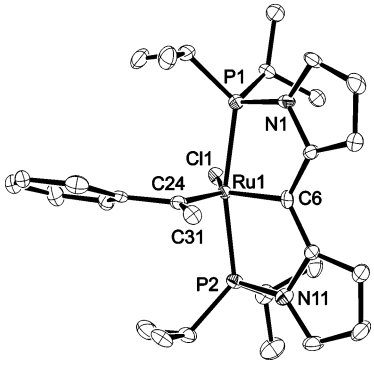


Figure 2. Thermal ellipsoid (50% probability) drawing of **10**.[27] All H atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1−C6, 1.911(4); Ru1−C24, 2.052(4); Ru1−P1, 2.3191(11); Ru1−P2, 2.3355(11); Ru1−Cl1, 2.4288(11); C6−Ru1−C24, 87.45(16); C6−Ru1−P1, 84.22(13); C24−Ru1−P1, 93.25(11); C6−Ru1−P2, 83.97(13); C24−Ru1−P2, 93.15(11); P1−Ru1−P2, 166.29(4); C6−Ru1−Cl1, 130.50(12); C24−Ru1−Cl1, 142.03(12); P1−Ru1−Cl1, 90.19(4); P2−Ru1−Cl1, 92.20(4).

The structure of **7a** was found to be approximately octahedral about Ru, with two carbonyl groups cis to each other and the C−H bond (of Ru−CH) anti to the Ru−Cl bond. The single Ru−C6 bond in **7a** (2.208(6) Å) is markedly longer than the Ru−$C_{carbene}$ double bonds in **2** and **10** (1.91−1.92 Å). Strikingly, the two Ru−CO bond distances are quite different (Ru−C25 is ca. 0.12 Å shorter than Ru−C24); we view this as a manifestation of the greater trans influence of CH (alkyl) vs Cl.

Catalytic Transfer Hydrogenation of Ketones. Several Ru complexes, including pincer-supported complexes, have been

(25) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(26) (a) Lam, W. H.; Shimada, S.; Batsanov, A. S.; Lin, Z.; Marder, T. B.; Cowan, J. A.; Howard, J. A. K.; Mason, S. A.; McIntyre, G. J. *Organometallics* **2003**, *22*, 4557. (b) Ferrando-Miguel, G.; Coalter, J. N., III; Gerard, H.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2002**, *26*, 687. (c) Rachidi, I. E.-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671. (d) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pelissier, M. *Organometallics* **1992**, *11*, 729. (e) Olivan, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1997**, *16*, 2227.

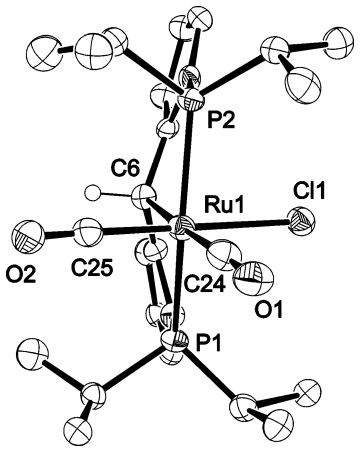
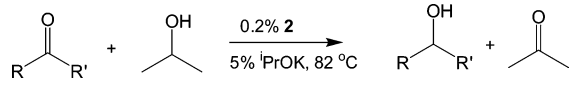


Figure 3. Thermal ellipsoid (50% probability) drawing of **7a**.[27] All H atoms were omitted for clarity (except for the one on C6). Selected bond distances (Å) and angles (deg): Ru1−C25, 1.835(7); Ru1−C24, 1.951(7); Ru1−C6, 2.208(6); Ru1−P1, 2.3482(18); Ru1−P2, 2.3591(17); Ru1−Cl1, 2.4433(18); C25−Ru1−C24, 89.1(3); C25−Ru1−C6, 93.6(3); C24−Ru1−C6, 176.8(3); C25−Ru1−P1, 94.0(2); C24−Ru1−P1, 99.8(2); C6−Ru1−P1, 81.55(18); C25−Ru1−P2, 94.3(2); C24−Ru1−P2, 97.2(2); C6−Ru1−P2, 80.99(17); P1−Ru1−P2, 161.06(6); C25−Ru1− Cl1, 179.4(2); C24−Ru1−Cl1, 90.3(2); C6−Ru1−Cl1, 86.91(18); P1−Ru1−Cl1, 86.34(6); P2−Ru1−Cl1, 85.44(6).

Scheme 11



shown to catalyze the transfer hydrogenation of ketones.[28−30] Compound **2** was found to be a precatalyst for the hydrogenation of ketones with 2-propanol as the hydrogen source and ^{i}PrOK as the base (Scheme 11). The results obtained are summarized in Table 1. The activity of **2** as a precatalyst is moderate when compared to other Ru pincer catalysts. However, these results show the competence of a (P_2C═) complex in a catalytic process.

Discussion

Structural Trends. The new (P_2C═) ligand demonstrates a pronounced preference for a meridional coordination to Ru. In all compounds investigated in this report, the two phosphine arms of the (P_2C═) ligand are in a trans disposition, as evidenced by the observation of appropriate virtual coupling to the two ^{31}P nuclei in solution and by the X-ray diffraction studies in the solid state on select compounds.

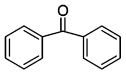
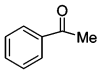
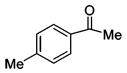
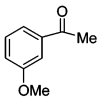
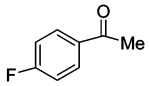
(27) Thermal ellipsoid plots were created using Ortep-3 for Windows: Farugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(28) For reviews relevant to the transfer hydrogenation of ketones, see: (a) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97. (c) Palmer, M. J.; Wills, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2045.

(29) For examples of pincer Ru complexes used as catalysts for transfer hydrogenation of ketones, see: (a) Deng, H.; Yu, Z.; Dong, J.; Wu, S. *Organometallics* **2005**, *24*, 4110. (b) Baratta, W.; Chelucci, G.; Gladiali, S.; Siega, K.; Toniutti, M.; Zanette, M.; Zangrando, E.; Rigo, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 6214. (c) Amoroso, D.; Jabri, A.; Yap, G. P. A.; Gusev, D. G.; dos Santos, E. N.; Fogg, D. E. *Organometallics* **2004**, *23*, 4047. (d) Albrecht, M.; Kocks, B. M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **2001**, *624*, 271. (e) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 743.

(30) Other examples of Ru-catalyzed transfer hydrogenation: (a) Cadierno, V.; Crochet, P.; Diez, J.; Garcia-Garrido, S. E.; Gimeno, J. *Organometallics* **2004**, *23*, 4836. (b) Brandt, P.; Roth, P.; Andersson, P. G. *J. Org. Chem.* **2004**, *69*, 4885. (c) Liu, P. N.; Gu, P. M.; Wang, F.; Tu, Y. Q. *Org. Lett.* **2004**, *6*, 169.

Table 1. Results for Hydrogenation of Ketones Using 2 as Catalyst

Entry	Ketones	Time (h)	Yield[a] (%)
1		3	85(82)
2		3	86(74)
3		3	76(72)
4		4	82 (74)[b]
5		3	87(75)
6		1.5	98

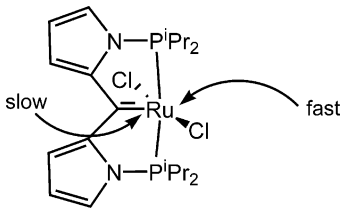
[a] GC yields. Isolated yields are shown in parentheses. [b] 3-Methoxyphenyl isobutyl ketone was also isolated in ca. 4% yield.

From the solid-state structural data on **2** and **10**, it appears that the two pyrrolyl rings of the ligand as well as the central carbene carbon are close to being coplanar. This is in contrast to the complexes of the diarylamido-based PNP ligands, where the six-membered aromatic rings are typically considerably twisted out of coplanarity. It is possible that the π conjugation of the aromatic rings with the central atom is more important and/or efficient in the (P_2C═) complexes than in the PNP complexes; conjugation obviously favors coplanarity. An alternative explanation is that the unfavorable steric interaction between the two ortho hydrogens is less pronounced in the dipyrrolylcarbene fragment (because of the smaller ring size) compared with the diphenylamide fragment.

Analysis of the Addition of Ligands to 2. In the addition of simple η^1 donors to **2**, two extreme situations were realized. Addition of hard, predominantly σ donor ligands such as MeCN and pyridine led to the formation of simple 18-electron, octahedral adducts. Two isomers were identified for the MeCN adduct (**3a**/**3b**), presumably differing by whether the MeCN ligand is trans to H or to carbene. The isomers are in equilibrium, given that the exchange between them occurs on the NMR time scale at ambient temperature. Both H and carbene are strong trans-influence ligands, and both Cl and MeCN (or pyridine in **4a**/**4b**) are weak trans-influence ligands. Thus there is a strong preference *not* to place H trans to carbene. On the other hand, apparently, the choice of exactly which weak trans-influence ligand (Cl or MeCN) is trans to which strong trans-influence ligand (H or carbene) is not especially important.

In the formation of bimetallic compounds **5** and **6**, the situation is similar. H and carbene are cis to each other, and there is a bridging chloride trans to each of them. The two bridging chlorides are equivalent, making only one isomer possible. Clearly, the bridging chloride is a weak trans-influence

Scheme 12



12

ligand, and thus, the outcome is similar to the addition of MeCN or pyridine: simple formation of an 18-electron adduct of a cis hydrido carbene.

At the other extreme is the reaction of **2** with CO. Addition of CO induces the migration of H to the carbene and coordination of two CO ligands. Migration of hydride to carbene[15b,31] or carbyne[32] under the influence of CO has been described in other systems. Factors influencing the balance among alkyl, carbene, and carbyne isomers have been reviewed.[33] Coordination of strong π acids such as CO should decrease the ability of Ru to stabilize the carbene p orbital by back-donation. This destabilization is alleviated by the migration of the hydride ligand. Another perspective on this is that hydride migration allows for coordination of two ligands (here CO) instead of one. Thus, the hydride migration should be induced by incoming ligands making strong bonds to Ru.

Trimethylphosphine may be viewed as intermediate in properties (in terms of softness and π acidity) between CO and MeCN. Accordingly, reaction of PMe_3 with **2** gives a mixture of products of the type observed for both CO (**9**, hydride migration) and MeCN (**8a**/**8b**, simple adduct). However, addition of ethylene results in the formation of only a simple adduct with the ethylene ligand bound trans to H (NMR evidence). The adduct formation is incomplete under 1 atm of C_2H_4 at -70 °C. This indicates that ethylene binds rather weakly to Ru and is consistent with the absence of the product with two ethylene ligands bound with concomitant hydride migration (analogous to **9**). Addition of phenylacetylene leads to insertion of the alkyne into the Ru−H bond instead of formation of an adduct. The greater preference for insertion for an alkyne vs an alkene can be explained by the weaker π bond in alkynes. It is notable that the carbene moiety is preserved in this reaction.

Formation and Isomerization of CO Adducts 14a to 14b. Addition of CO to **12** leads only to simple adduct formation, in contrast to CO addition to **2**. The adducts **14a**/**14b** are quite thermally robust in terms of preserving the *mer*-(P_2C═) ligand intact. Compound **14a** is the kinetically preferred product of addition of CO to **12**. In the presumed approximately square-pyramidal geometry of **12** the LUMO of the molecule should approximately correspond to the empty site trans to the carbene ligand, and this is the site of the kinetically preferred attack by an incoming CO (Scheme 12). The isomerization of **14a** to **14b** proceeds slowly, even at >100 °C, and may require dissociation of CO and slow attack on the position cis to carbene.

The CO ligand in **14a** is placed trans to the carbene. In **14b**, CO is trans to a chloride. It seems reasonable to posit that the Ru−CO interaction would be stronger when CO is trans to a chloride (weak trans influence ligand) than when it is trans to the carbene (strong trans influence ligand). This reasoning is supported by the IR spectroscopic data: the CO stretching vibration in **14b** (ν_{CO} 1967 cm^{-1}) is indicative of a greater degree of back-donation than in **14a** (ν_{CO} 1991 cm^{-1}). The preference for the cis disposition of the two stong π acids in **14b** is probably the reason for its higher thermodynamic stability.[34]

Conclusion

The P_2CH_2 precursor to the new (P_2C═) pincer ligand can be synthesized in a straightforward fashion from readily available materials. Here we demonstrate that double C−H activation in P_2CH_2 easily leads to (P_2C═)Ru complexes. The (P_2C═) ligand displays a pronounced preference to bind to Ru in a meridional fashion, and its carbene moiety is preserved in most reactions studied here. The only instances where the carbene was compromised involved migration of a metal-bound hydride to the carbene under the influence of coordination of strongly binding ligands such as PMe_3 and CO. However, even in these cases, the phosphine arms remain bound, perhaps owing to the rigidity of the chelate backbone. On the other hand, CO addition to (P_2C═)$RuCl_2$ (**12**), a complex devoid of Ru−H, occurs with preservation of the carbene functionality, even at >100 °C. Furthermore, insertion of phenylacetylene into the Ru−H bond of (P_2C═)RuHCl proceeds with retention of the carbene moiety, demonstrating that organometallic transformations at the Ru center are indeed possible without the direct involvement of the carbene, which remains part of the spectator pincer ligand. The increasing recognition of pincer ligands stems largely from their ability to form very robust metal complexes. All in all, (P_2C═) appears to be a promising, and electronically distinctive, addition to this class of ligands.

Experimental Section

General Considerations. Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Toluene, pentane, Et_2O, C_6D_6, C_6H_6, THF, and isooctane were dried over NaK/Ph_2-CO/18-crown-6, distilled, or vacuum-transferred and stored over molecular sieves in an Ar-filled glovebox. Dipyrromethane was prepared according to the literature procedures.[18] All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 (^{1}H NMR, 399.755 MHz; ^{13}C NMR, 100.518 MHz; ^{31}P NMR, 161.822 MHz; ^{2}H, 61.365 MHz) spectrometer. For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ). GC/MS spectra were recorded on a Hewlett-Packard G1800C GCD System (GCD plus gas chromatograph electron ionization detector) employing HP-5MS from Agilent Technologies (30 m (column length) × 0.25 mm (i.d.)) and 1227032 from J & W Scientific (30 m × 0.250 mm). Helium was used as a carrier gas.

***N,N′*-Bis(diisopropylphosphino)dipyrromethane (P_2CH_2, 1).** To a solution of dipyrromethane (783 mg, 5.36 mmol) in THF (20 mL) was slowly added NaH (643 mg, 26.8 mmol). The mixture was stirred for 2 h, and then ClP^iPr_2 (1.71 mL, 10.72 mmol) was added all at once. The resulting mixture was stirred for 10 h. All

(31) (a) Lee, J.-H.; Pink, M.; Caulton, K. G. *Organometallics* **2006**, *25*, 802. (b) Winter, M. J. *Polyhedron* **1989**, *8*, 1583.

(32) (a) Bolano, T.; Castarlenas, R.; Esteruelas, M. A.; Modrego, F. J.; Onate, E. *J. Am. Chem. Soc*. **2005**, *127*, 11184. (b) Bannwart, E.; Jacobsen, H.; Furno, F.; Berke, H. *Organometallics* **2000**, *19*, 3605. (c) Spivak, G. J.; Caulton, K. G. *Organometallics* **1998**, *17*, 5260.

(33) Caulton, K. G. *J. Organomet. Chem*. **2001**, *617*−*618*, 56.

(34) Nelson et al. determined that the cis positioning of two π acids (CO's) is thermodynamically favored in $(R_3P)_2RuCl_2(\pi\text{-acid})_2$. Our compound is also generically $(R_3P)_2RuCl_2(\pi\text{-acid})_2$, where $(\pi\text{-acid})_2$ = carbene + CO. (a) Krassowski, D. W.; Nelson, J. H.; Brower, K. R.; Hauenstein, D.; Jacobson, R. A. *Inorg. Chem.* **1988**, *27*, 4294. (b) Krassowski, D. W.; Reimer, K.; LeMay, H. E.; Nelson, J. H. *Inorg. Chem.* **1988**, *27*, 4307.

volatiles were removed under vacuum, and the residue was extracted with ether and passed through a pad of Celite. The product was isolated as a viscous colorless liquid by evaporation and drying of the resultant liquid under vacuum for 1 h. Yield: 1.88 g (93%). ^{1}H NMR (C_6D_6): δ 6.62 (br s, 2H, py *H*), 6.39 (m, 2H, py *H*), 6.19 (br s, 2H, py *H*), 4.59 (s, 2H, $-CH_2-$), 1.82 (m, 4H, C*H*Me$_2$), 0.92 (dd, 12H, J = 7 Hz, J = 16 Hz, 12H, CH*Me*$_2$), 0.87 (dd, 12H, J = 7 Hz, J = 16 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 138.7 (d, J = 19 Hz), 121.7 (d, J = 7 Hz), 111.1 (s), 110.0 (s), 27.7 (d, J = 15 Hz, *C*HMe$_2$), 27.2 (t, J = 19 Hz, $-CH_2-$), 19.1 (d, J = 24 Hz, CH*Me*$_2$), 18.9 (d, J = 11 Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 56.8 (s). GC/MS data: *m*/*z* 378 (M^+), 335 ($M^+ - C_3H_7$), 261 ($M^+ - PC_6H_{14}$), 217, 175.

(P_2C═)Ru(H)(Cl) (2). A mixture of $[RuCl_2(p\text{-cymene})]_2$ (307 mg, 1.00 mmol Ru), **1** (400 mg, 1.06 mmol), and Et_3N (1.40 mL, 10 mmol) in 15 mL of toluene was stirred for 12 h at 100 °C. Then, the mixture was filtered and all volatiles were removed under vacuum. The resulting dark red solid was further purified by recrystallization in toluene/pentane solution at −35 °C. Yield: 390 mg (75%). ^{1}H NMR (C_6D_6): δ 6.91 (br s, 2H, py *H*), 6.72 (d, 2H, J = 3 Hz, py *H*), 6.39 (t, J = 3 Hz, 2H, py *H*), 2.74 (m, 2H, C*H*Me$_2$), 2.08 (m, 2H, C*H*Me$_2$), 1.19 (dvt, app quartet, J_{H-P} = 8 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$), 1.11 (dvt, app quartet, J_{H-P} = 8 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$), 0.98 (m, 12 H, CH*Me*$_2$), −15.3 (t, J = 18.3 Hz, 1H, Ru−H). ^{13}C{^{1}H} NMR (C_6D_6): δ 253.0 (t, J = 8 Hz, Ru═*C*), 159.6 (t, J = 15 Hz), 127.5 (m, overlap with solvent resonance signal), 117.8 (s), 101.7 (t, J = 4 Hz), 28.3 (t, J = 8 Hz, *C*HMe$_2$), 26.9 (t, J = 11 Hz, *C*HMe$_2$), 18.7 (s, CH*Me*$_2$), 18.0 (s, CH*Me*$_2$), 17.5 (t, J = 5 Hz, CH*Me*$_2$), 16.8 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 120.6 (s). Anal. Calcd for $C_{21}H_{35}ClN_2P_2Ru$: C, 49.07; H, 6.86; N, 5.45. Found: C, 49.19; H, 6.75; N, 5.36.

(P_2C═)Ru(H)(Cl)(NCCH$_3$) (3a/3b). To a solution of **2** (38 mg, 0.074 mmol) in 5 mL of toluene was added CH_3CN (20 μL, 0.367 mmol). Then, the mixture was stirred for 10 min. ^{31}P NMR in situ indicated a complete conversion to (P_2C═)Ru(H)(Cl)(NCCH$_3$). The title compound was isolated as a red solid after the removal of all volatiles. ^{1}H NMR (C_6D_6, 298 K): δ 6.94 (m, 2H, py *H*), 6.71 (dd, J = 1.2 Hz, J = 4 Hz, 2H, py *H*), 6.41 (m, 2H, py *H*), 2.69 (m, 2H, C*H*Me$_2$), 2.12 (m, 2H, C*H*Me$_2$), 1.31 (dvt, app quartet, J_{H-P} = 8 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$), 1.21 (dvt, app quartet, J_{H-P} = 9 Hz, J_{H-H} = 7 Hz, 6H, CH*Me*$_2$), 1.09 (dvt, app quartet, J_{H-H} = 7 Hz, J_{H-P} = 8 Hz, 6H, CH*Me*$_2$), 0.98 (dvt, app quartet, J_{H-H} = 8 Hz, J_{H-P} = 7 Hz, 6H, CH*Me*$_2$), 0.58 (s, 3 Hz, Ru−NCC*H*$_3$), −13.2 (br s, 1H, Ru−*H*). ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.36 (m, 2H, py *H*), 6.62 (dd, J = 1.2 Hz, J = 3.6 Hz, 2H, py *H*), 6.51 (dd, 2H, J = 2.6 Hz, J = 4 Hz, py H), 2.86 (m, 2H, C*H*Me$_2$), 2.50 (m, 2H, C*H*Me$_2$), 2.12 (s, 3H, Ru−NCCH$_3$), 1.42 (dvt, app quartet, J_{H-P} = 7.2 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$), 1.28 (dvt, app quartet, J_{H-P} = 7.3 Hz, J_{H-H} = 7.2 Hz, 6H, CH*Me*$_2$), 1.26 (dvt, app quartet, J_{H-H} = 6.9 Hz, J_{H-P} = 6.9 Hz, 6H, CH*Me*$_2$), 0.92 (dvt, app quartet, J_{H-H} = 7.2 Hz, J_{H-P} = 7.6 Hz, 6H, CH*Me*$_2$), −10.5 (t, 1H, J = 20 Hz, Ru−H). ^{13}C{^{1}H} NMR (C_6D_6): δ 252.7 (t, J = 8 Hz, Ru═C), 159.4 (t, J = 10 Hz), 128.8 (s, RuN*C*CH$_3$), 127.1 (m, overlap with solvent resonance signal), 117.9 (s), 101.6 (t, J = 4 Hz), 29.1 (t, J = 9 Hz, *C*HMe$_2$), 28.3 (t, J = 11 Hz, *C*HMe$_2$), 18.7 (s, CH*Me*$_2$), 18.1 (t, J = 3 Hz, CH*Me*$_2$), 17.9 (t, J = 6 Hz, CH*Me*$_2$), 17.5 (s, CH*Me*$_2$), 0.50 (s, Ru−NC*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 120.3 (s). Anal. Calcd for $(C_{23}H_{38}ClN_3P_2Ru)\cdot(C_5H_{12})_{0.1}$: C, 50.20; H, 7.03. Found: C, 50.12; H, 7.07. Selected NMR data for **3b** (major isomer) at −65 °C: ^{1}H NMR (CD_2Cl_2) δ −10.6 (t, J = 19 Hz, Ru−*H*). Selected NMR data for **3a** (minor isomer) at −65 °C: ^{1}H NMR (CD_2Cl_2) δ −9.2 (t, J = 19 Hz, Ru−*H*).

(P_2C═)Ru(H)(Cl)(pyridine) (4a/4b). A mixture of **2** (30 mg, 0.058 mmol) with pyridine (25 μL, 0.292 mmol) was stirred in C_6D_6 for 5 min. Then, all volatiles were removed under vacuum. The resulting solid was washed with pentane and dried in vacuo. ^{1}H NMR ($CDCl_3$): δ 9.91 (br s, 1H, py *H*), 7.97 (br s, 1H, py *H*), 7.53 (t, J = 8 Hz, 1H, py *H*), 7.24 (m, 3H, two peaks overlapping), 6.94 (br s, 1H, py *H*), 6.72 (d, J = 2 Hz, 2H, py *H*), 6.50 (t, J = 2.8 Hz, 2H, py *H*), 2.50 (br s, 2H, PC*H*Me$_2$), 2.40 (br t, 2H, J = 6.8 Hz, PC*H*Me$_2$), 1.32 (br s, 6H, PCH*Me*$_2$), 1.10 (dvt, app quartet, J_{H-H} = 7.6 Hz, J_{H-P} = 7.6 Hz, 6H), 0.94 (dvt, app quartet, J_{H-H} = 6.8 Hz, J_{H-P} = 6.8 Hz, 6H), 0.46 (br s, 6H, PCH*Me*$_2$), −9.12 (t, J = 21.6 Hz, 1H, Ru−H). ^{1}H NMR (CD_2Cl_2, 22 °C): δ −9.25 (t, J = 21.6 Hz, 1H, Ru−H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 250.0 (br, Ru═C), 158.8 (t, J = 14 Hz), 153.2 (br), 136.7 (s), 127.7 (s), 124.6 (s), 117.9 (s), 101.2 (s), 32.0 (br, *C*HMe$_2$), 31.0 (br, *C*HMe$_2$), 18.8 (br, CH*Me*$_2$), 18.3 (s, CH*Me*$_2$), 18.1 (s, CH*Me*$_2$), 17.6 (t, J = 4 Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 117.7 (s). Two distinct isomers were observed in CD_2Cl_2 at −60 °C in a 11:1 ratio. NMR data for **4b** (major isomer) at −60 °C: ^{1}H NMR (CD_2Cl_2) δ 9.75 (d, J = 5 Hz, 1H, py *H*), 7.86 (d, J = 4 Hz, 1H, py *H*), 7.58 (t, J = 8 Hz, 1H, py *H*), 7.32 (t, J = 6 Hz, 1H, py *H*), 7.29 (br, s, 2H, py *H*), 6.90 (t, J = 7 Hz, 2H, py *H*), 6.74 (br, s, 2H, py *H*), 6.52 (m, 2H, py *H*), 2.47 (br, s, 2H, C*H*Me$_2$), 2.35 (m, 2H, C*H*Me$_2$), 1.22 (app q (dvt), J = 8 Hz, J = 14 Hz, 6H, CH*Me*$_2$), 1.11 (m, 6H, CH*Me*$_2$), 0.85 (m, 6H, CH*Me*$_2$), 0.26 (app q (dvt), J = 6 Hz, J = 14 Hz, 6H, CH*Me*$_2$), −9.23 (t, J = 21 Hz, Ru−*H*); ^{31}P {^{1}H} NMR (CD_2Cl_2, 213 K) δ 119.0 (s). NMR data for **4a** (minor isomer) at −60 °C: ^{1}H NMR (CD_2Cl_2) δ −9.69 (t, J = 19 Hz, Ru−*H*); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 119.3 (s).

NMR Reaction of (P_2C═)Ru(H)(Cl) with $[RuCl_2(p\text{-cymene})]_2$. A J. Young NMR tube was charged with **2** (23 mg 0.0447 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (14 mg, 0.0447 mmol of Ru) in 0.5 mL of C_6D_6. NMR in situ revealed a mixture of (P_2C═)Ru(H)(Cl) (**2**) along with **5** and $[Ru(p\text{-cymene})Cl_2]_2$ (72% conversion, presumably in an equilibrium). Selected NMR data for **5** are as follows. ^{1}H NMR (C_6D_6): δ 6.98 (br, s, 2H, py *H*), 6.62 (br, s, 2H, py *H*), 6.38 (br, s, 2H, py *H*), 5.24 (d, J = 5.6 Hz, 2H, *p*-cymene), 4.81 (d, J = 6.0 Hz, 2H, *p*-cymene), 2.71 (m, 2H, C*H*Me$_2$), 2.40 (m, 2H, C*H*Me$_2$), 1.71 (s, 3H, *p*-cymene), 1.55 (br, 6H, CH*Me*$_2$), 1.29 (br, 6H, CH*Me*$_2$), 1.21 (br, 6H, CH*Me*$_2$), 1.10 (d, J = 6.4 Hz, 6H, *p*-cymene), −11.5 (t, J = 19.2 Hz, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 121.0 (br, s).

[(P_2C═Ru)(H)](μ-Cl)$_2$[Rh(COD)] (6). A solution of **2** (60 mg, 0.11 mmol) and $[Rh(COD)Cl]_2$ (28.4 mg, 0.11 mmol of Rh) in 5 mL of toluene was stirred at room temperature for 30 min. Then all volatiles were removed under vacuum. The resulting solid was washed with pentane and dried under vacuum. Yield: 63 mg (75%). ^{1}H NMR (C_6D_6): δ 6.97 (br s, 2H, py *H*), 6.61 (d, J = 3.6 Hz, 2H, py *H*), 6.40 (t, J = 3.6 Hz, 2H, py *H*), 4.21 (s, 4H, C*H* of COD), 3.31 (m, 2H, PC*H*Me$_2$), 2.27 (m, 2H, PC*H*Me$_2$), 2.20 (br s, 4H, CH_2 of COD), 1.80 (dvt, app quartet, J = 7.6 Hz, J = 7.6 Hz, 6H, PCH*Me*$_2$), 1.47 (dvt, app quartet, J = 6.4 Hz, J = 6.8 Hz, 6H, PCH*Me*$_2$), 1.38 (dvt, app quartet, J = 7.2 Hz, J = 6.8 Hz, 6H, PCH*Me*$_2$), another part of the COD resonance signal overlaps with the two quartets at δ 1.47 and 1.38 ppm (integrated to 4H), 0.96 (dvt, app quartet, J = 7.2 Hz, J = 7.2 Hz, 6H, PCH*Me*$_2$), −10.6 (t, J = 20.4 Hz, Ru−*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 253.6 (t, J = 9.1 Hz), 159.0 (t, J = 14.4 Hz), 127.5 (s), 117.8 (s), 101.5 (t, J = 3.8 Hz), 78.5 (d, J_{C-Rh} = 13.6 Hz, *C*H of COD), 78.3 (d, J_{C-Rh} = 13.6 Hz, *C*H of COD), 31.1 (s, CH_2 of COD), 30.4 (t, J = 11.5 Hz, PC*H*Me$_2$), 30.5 (t, J = 11.5 Hz, PC*H*Me$_2$), 18.9 (t, J = 2.3 Hz, PCH*Me*$_2$), 18.8 (s, PCH*Me*$_2$), 18.6 (s, PCH*Me*$_2$), 18.5 (t, J = 4.6 Hz, PCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 117.8 (s).

(P_2CH)Ru(Cl)(CO)$_2$ (7a/7b). A J. Young NMR tube was charged with **2** (20 mg, 0.039 mmol) and 0.5 mL of C_6D_6. After three freeze−pump−thaw cycles, 1 atm CO was introduced (~0.090 mmol). The color changed from dark red to pale greenish immediately. All volatiles were removed under vacuum. The yield for the major isomer is 92% when monitored in situ by ^{31}P NMR (with 8% minor isomer). Attempts to separate the isomers by recrystallization from various solvents were unsuccessful. NMR

data for the major isomer are as follows. ^{1}H NMR (C_6D_6): δ 6.55 (m, 4H, py *H*), 6.36 (br s, 2H, py *H*), 5.08 (br s, 1H, Ru−C*H*), 2.92 (m, 2H, PC*H*Me$_2$), 2.15 (m, 2H, PC*H*Me$_2$), 1.48 (dvt, app quartet, J_{H-H} = 9 Hz, J_{H-P} = 7.6 Hz, 6H), 1.12 (dvt, app quartet, J_{H-H} = 7.6 Hz, J_{H-P} = 7.2 Hz, 6H, PCH*Me*$_2$), 0.92 (dvt, app quartet, J_{H-H} = 9.6 Hz, J_{H-P} = 7.2 Hz, 6H, PCH*Me*$_2$), 0.77 (dvt, app quartet, J_{H-H} = 8 Hz, J_{H-P} = 7.2 Hz, 6H, PCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 199.2 (t, J = 13 Hz, Ru−CO), 194.5 (t, J = 8 Hz, Ru−CO), 150.7 (vt, J = 10.4 Hz), 117.3 (s), 116.0 (s), 107.4 (br s), 31.0 (vt, J = 12.3 Hz, P*C*HMe$_2$), 29.2 (vt, J = 13.3 Hz, P*C*HMe$_2$), 25.2 (br s, RuCH), 22.2 (s, PCH*Me*$_2$), 18.9 (s, PCH*Me*$_2$), 17.6 (br s, PCH*Me*$_2$), 17.3 (s, PCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 114.5 (s). ν_{CO} (toluene): 2028 and 1954 cm^{-1}. Selected NMR data for the minor isomer: ^{31}P{^{1}H} NMR (C_6D_6) δ 114.6 (s, a shoulder peak); ^{1}H NMR (C_6D_6) 5.26 (s, Ru−CH).

NMR Reaction of (P_2C═)Ru(H)(Cl) with PMe_3 (1.2 Equiv). A J. Young NMR tube was charged with **2** (27 mg, 0.0525 mmol), PMe_3 (7 μL, 0.063 mmol), and 0.5 mL of C_6D_6. The solution turned an intense purple. Three compounds, (P_2C═)Ru(H)(Cl)(PMe_3) (50%) (**8b**, major isomer: H trans to Cl), (P_2C═)Ru(H)(Cl)(PMe_3) (17%) (**8a**, minor isomer: H trans to PMe_3), and (PCHP)Ru(Cl)-(PMe_3)$_2$ (33%) (**9**, two PMe_3 groups cis to each other), as well as free PMe_3 were observed.

NMR Reaction of (P_2C═)Ru(H)(Cl) with Excess PMe_3 (5 Equiv). A J. Young NMR tube was charged with **2** (15 mg, 0.029 mmol), PMe_3 (7 μL, 0.15 mmol), and 0.5 mL of C_6D_6. The solution turned a very intense purple. NMR indicates that the mixture consists of **8b** (3%) and **9** (97%) as well as free PMe_3. Selected NMR data for (P_2C═)Ru(H)(Cl)(PMe_3) (**8b**): ^{1}H NMR (C_6D_6) δ 6.94 (d, J = 2.4 Hz, 2H, py *H*), 6.82 (d, J = 3.6 Hz, 2H, py *H*), 6.63 (t, J = 3.2 Hz, 2H, py *H*), −12.6 (dt, J_{H-PMe_3} = 29.3 Hz, J_{H-PiPr_2} = 18.3 Hz, 1H); ^{31}P{^{1}H} NMR (C_6D_6) δ 126.2 (d, J = 13.0 Hz, P^{i}Pr$_2$), −23.7 (m). ^{13}C{^{1}H} NMR (C_6D_6): δ 245.4 (dt, J_{C-PMe_3} = 69.2 Hz, J_{C-PiPr_2} = 11 Hz, Ru═C). Selected NMR data for (P_2C═)Ru(H)(Cl)(PMe_3) (**8a**): ^{1}H NMR (C_6D_6) δ 7.11 (d, J = 2.4 Hz, 2H, py *H*), 6.54 (d, J = 3.2 Hz, 2H, py *H*), 6.37 (t, J = 3.0 Hz, 2H, py *H*), −3.96 (dt, J_{H-PMe_3} = 104.3 Hz, J_{H-PiPr_2} = 27.0 Hz); ^{31}P{^{1}H} NMR (C_6D_6) δ 124.2 (d, J = 32.8 Hz, P^{i}Pr$_2$), −24.0 (t, J = 28.5 Hz); ^{13}C{^{1}H} NMR (C_6D_6) δ 253.4 (m, Ru═C). Selected NMR data for (PCHP)Ru(Cl)(PMe_3)$_2$ (**9**): ^{1}H NMR (C_6D_6) δ 6.65 (s, 2H, py *H*), 6.63 (t, J = 3.0 Hz, 2H, py *H*), 6.57 (s, 2H, py *H*), 5.80 (br, d, J = 5.2 Hz, Ru−C*H*, 1H); ^{31}P{^{1}H} NMR (C_6D_6) δ 113.9 (dd, J = 13.8 Hz, J = 34.6 Hz, P^{i}Pr$_2$), 7.1 (m, PMe_3), −25.4 (m, PMe_3).

(P_2C═)Ru(CPh═CH_2)(Cl) (10). A mixture of **2** (88 mg, 0.17 mmol) with PhC≡CH (190 μL, 1.71 mmol) was stirred in toluene for 5 min. The title product was formed quantitatively, on the basis of ^{31}P NMR spectra. Then all volatiles were removed under vacuum. X-ray-quality crystals were grown from a toluene/pentane saturated solution at −35 °C. ^{1}H NMR (C_6D_6): δ 7.95 (d, J = 8 Hz, 2H, C*H* of Ph), 7.21 (t, J = 8 Hz, 2H, C*H* of Ph), 7.06 (t, J = 8 Hz, 1H, C*H* of Ph), 6.91 (d, J = 2 Hz, 2H, py *H*), 6.87 (d, J = 3 Hz, 2H, py *H*), 6.43 (t, J = 4 Hz, 2H, py *H*), 5.48 (s, 1H, PhC═C*H*$_2$), 4.23 (s, 1H, PhC═C*H*$_2$), 3.10 (m, C*H*Me$_2$), 2.44 (m, C*H*Me$_2$), 0.99−0.93 (m, 18H, CH*Me*$_2$), 0.88 (dvt, app quartet, J_{H-H} = 6.4 Hz, J_{H-P} = 6.4 Hz, 6H). ^{13}C{^{1}H} NMR (C_6D_6): δ 253.0 (t, J = 9 Hz, Ru═*C*), 162.1 (br), 158.0 (vt, J = 13.5 Hz), 144.2 (s), 128.7 (s), 127.5 (s), 127.4 (s), 124.1 (s), 117.7 (s), 114.7 (s), 103.3 (s), 27.8 (vt, J = 9 Hz, *C*HMe$_2$), 27.3 (vt, J = 9.7 Hz, *C*HMe$_2$), 18.5 (s), 18.3 (s), 16.2 (s), 16.1 (vt, J = 3 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 106.7 (s).

(P_2C═)Ru(H)(Cl)(C_2H_4) (11). A J. Young NMR tube was charged with **2** (20 mg, 0.039 mmol) and 0.5 mL of C_6D_6. After three freeze−pump−thaw cycles, 1 atm of ethylene was introduced (∼0.090 mmol). ^{31}P NMR and ^{1}H NMR data suggest the coordination of ethylene to the Ru metal center. ^{1}H NMR (C_6D_6): δ 6.98 (d, J = 1.6 Hz, 2H, py *H*), 6.56 (d, J = 3.2 Hz, 2H, py *H*), 6.36 (t, J = 3.2 Hz, 2H, py *H*), 4.47 (br s, Ru−(η^2-C_2H_4)), 2.76 (m, 2H, PC*H*Me$_2$), 2.17 (m, 2H, PC*H*Me$_2$), 1.34 (m, 12H, PCH*Me*$_2$), 1.23 (dvt, app quartet, J_{H-H} = 7.6 Hz, J_{H-P} = 7.2 Hz, 6H), 0.78 (dvt, app quartet, J_{H-H} = 7.6 Hz, J_{H-P} = 7.2 Hz, 6H), −4.0 (br, Ru−H). ^{31}P{^{1}H} NMR (C_6D_6): δ 125.7 (s).

NMR Observations of the Reaction of 2 with Ethylene at Low Temperature. A J. Young NMR tube was charged with **2** (20 mg, 0.039 mmol) and 0.5 mL of CD_2Cl_2. After three freeze−pump−thaw cycles, 1 atm of ethylene was introduced (∼0.090 mmol). ^{1}H NMR spectra were measured at the following temperatures (K): 298, 283, 268, 253, 238, 223, 208, and 202. At 202 K, the resonance signals for **2** and **11** were observed and well resolved. NMR data for **11**: ^{1}H NMR (CD_2Cl_2, 202 K) δ 7.50 (s, 2H, py *H*), 6.85 (d, J = 3.2 Hz, py *H*), 6.66 (t, 2H, J = 2.4 Hz, py *H*), 3.20 (br, 2H, C*H*Me$_2$), 3.13 (s, 4H, Ru−C_2H_4), 2.69 (m, 2H, C*H*Me$_2$), 1.64 (dvt, app quartet, J_{H-P} = 6.4 Hz, J_{H-H} = 6.8 Hz, 6H, CH*Me*$_2$), 1.56 (dvt, app quartet, J_{H-P} = 7.6 Hz, J_{H-H} = 8 Hz, 6H, CH*Me*$_2$), 1.29 (dvt, app quartet, J_{H-H} = 7.2 Hz, J_{H-P} = 9.2 Hz, 6H, CH*Me*$_2$), 0.55 (dvt, app quartet, J_{H-H} = 7.6 Hz, J_{H-P} = 7.2 Hz, 6H, CH*Me*$_2$), −3.82 (t, 1H, J = 25 Hz, Ru-*H*); ^{31}P NMR (CD_2Cl_2, 202 K) δ 127.1 (s).

(P_2C═)$RuCl_2$ (12). A mixture of **2** (100 mg, 0.194 mmol) and [Et_2N═CH_2]Cl (23 mg, 0.194 mmol) was stirred in 10 mL of toluene for 1 h. Then all volatiles were removed under vacuum, and the mixture was extracted with toluene and passed through a pad of Celite. The solution was evaporated, and the resulting solid was washed with pentane and dried under vacuum. Yield: 64 mg (60%). ^{1}H NMR (C_6D_6): δ 7.08 (br s, 2H, py *H*), 6.75 (d, J = 3.2 Hz, 2H, py *H*), 6.30 (t, J = 3.2 Hz, 2H, py *H*), 2.80 (m, 4H, PC*H*Me$_2$), 1.21 (m, 24H, PCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 255.1 (t, J = 8 Hz), 159.3 (vt, J = 13.7 Hz), 131.0 (vt, J = 2.3 Hz), 117.5 (s), 101.4 (vt, J = 3.8 Hz), 27.5 (vt, J = 10 Hz, PC*H*Me$_2$), 18.7 (s, PCH*Me*$_2$), 17.5 (vt, J = 2.3 Hz, PCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 99.0 (s). Anal. Calcd for ($C_{21}H_{34}Cl_2N_2P_2Ru$)(C_7H_8)$_{0.2}$: C, 47.46; H, 6.33. Found: C, 47.72; H, 6.06.

(P_2C═)$Ru(Ph)_2$ (13). A mixture of **12** (20 mg, 0.039 mmol) with a large excess of Ph_2Mg (50 mg, 0.19 mmol) was stirred in C_6D_6 for 10 h. The mixture was passed through a pad of Celite, and then all volatiles were removed under vacuum. The resulting solid was extracted with ether, and the ether extract was filtered and evaporated to afford the title compound. ^{1}H NMR (C_6D_6): δ 7.41 (d, J = 6.8 Hz, 4H, C*H* of Ph), 7.10 (t, J = 7.2 Hz, 4H, C*H* of Ph), 6.89 (t, J = 6.8 Hz, 2H, C*H* of Ph), 6.81 (m, 2H, py *H*), 6.77 (br, d, J = 2 Hz, 2H, py *H*), 6.45 (t, J = 3.2 Hz, 2H, py *H*), 2.19 (m, 4H, PC*H*Me$_2$), 0.78 (dvt, app quartet, J_{H-H} = 8 Hz, J_{H-P} = 7.6 Hz, 12H, PCH*Me*$_2$), 0.58 (dvt, app quartet, J_{H-H} = 6.8 Hz, J_{H-P} = 6.8 Hz, 12H, PCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 238.2 (t, J = 9.4 Hz, Ru═C), 178.2 (vt, J = 10.2 Hz, *C*H of Ph), 156.7 (vt, J = 14.8 Hz), 132.9 (br s, *C*H of Ph), 127.4 (m, overlap with solvent), 125.7 (vt, J = 2.2 Hz), 121.9 (s), 117.2 (s), 100.9 (vt, J = 4.2 Hz), 27.9 (vt, J = 10.2 Hz, PC*H*Me$_2$), 17.0 (vt, J = 3 Hz, PCH*Me*$_2$), 16.8 (s, PCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 102.8 (s).

(P_2C═)$Ru(Cl_2)$(CO) (14a/14b). A solution of **12** (40 mg, 0.073 mmol) in CH_2Cl_2 was stirred for 20 min under CO at ambient temperature. NMR in situ indicated the quantitative formation of **14a.** The dark green solution was stripped to dryness under vacuum to afford the product as a purple solid. **14a**: ^{1}H NMR (C_6D_6) δ 7.08 (s, 2H, py *H*), 6.86 (d, J = 3.7 Hz, 2H, py *H*), 6.31 (t, J = 3.1 Hz, 2H, py *H*), 3.00 (m, 4H, C*H*Me$_2$), 1.36 (dvt, app quartet, J_{H-H} = 8 Hz, J_{H-P} = 8 Hz, 12 H), 1.28 (dvt, app quartet, J_{H-H} = 7.6 Hz, J_{H-P} = 7.6 Hz, 12 H); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 256.1 (t, J = 8 Hz, Ru═*C*), 203.1 (t, J = 8.4 Hz, Ru−*C*O), 155.7 (vt, J = 12.6 Hz), 140.0 (s), 121.6 (s), 115.3 (vt, J = 3.8 Hz), 27.6 (vt, J = 10.1 Hz, *C*HMe$_2$), 20.0 (s), 18.6 (s); ^{31}P{^{1}H} NMR (C_6D_6) δ 126.1 (s); ν_{CO} (CH_2Cl_2) 1991 cm^{-1}. Compound **14b** was formed in 92% NMR yield when a solution of **14a** in toluene was heated at 110 °C for 5 days. **14b**: ^{1}H NMR (C_6D_6) δ 6.87 (br, s, 2H, py *H*), 6.67

(d, J = 3.6 Hz, 2H, py *H*), 6.23 (m, 2H, py *H*), 3.74 (m, 2H, C*H*Me$_2$), 2.46 (m, 2H, C*H*Me$_2$), 1.71 (dvt, app quartet, J_{H-H} = 9.2 Hz, J_{H-P} = 8.8 Hz, 6 H), 1.47 (dvt, app quartet, J_{H-H} = 9.2 Hz, J_{H-P} = 8.8 Hz, 6 H), 1.10 (dvt, app quartet, J_{H-H} = 6.8 Hz, J_{H-P} = 6.8 Hz, 6 H), 0.97 (dvt, app quartet, J_{H-H} = 7.2 Hz, J_{H-P} = 7.6 Hz, 6 H); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 239.9 (t, J = 8 Hz, Ru=*C*), 200.9 (t, J = 13 Hz, Ru−*C*O), 155.0 (vt, J = 11 Hz), 139.0 (s), 121.0 (s), 115.3 (vt, J = 3 Hz), 28.7 (vt, J = 9.1 Hz, *C*HMe$_2$), 28.2 (vt, J = 9.1 Hz, *C*HMe$_2$), 19.4 (vt, J = 3 Hz, CH*Me*$_2$), 18.6 (vt, J = 4.3 Hz, CH*Me*$_2$), 18.4 (s, CH*Me*$_2$), 18.2 (s, CH*Me*$_2$); ^{31}P-{^{1}H} NMR (C_6D_6) δ 113.1 (s); ν_{CO} (CH_2Cl_2) 1967 cm^{-1}.

Phenylacetylene Dimerization Reaction Catalyzed by 2. A screw-cap NMR tube was charged with phenylacetylene (58 μL, 0.529 mmol) and **2** (2.7 mg, 0.0053 mmol) in 0.50 mL of C_6D_6. Then PhC≡CLi (5.3 μL, 0.0053 mmol, 1 M in THF) was added. The mixture was heated at 110 °C and monitored by ^{1}H NMR. The resulting solution was passed through a pad of silica gel prior to analysis by GC/MS.

General Procedure for Catalytic Transfer Hydrogenation of Ketones. To a mixture of ketone (2 mmol), the catalyst **2** (0.004 mmol, 2 mL of a stock solution of **2** in ^{i}PrOH) and 2 mL of ^{i}PrOH was added a solution of ^{i}PrOK (196 μL of a 5 wt % solution in ^{i}PrOH, 0.1 mmol). The mixture was stirred at room temperature for 10 min. The mixture was then stirred in an oil bath that was preheated to 82 °C. The mixture turned pale yellowish after the reaction was complete. The solution was concentrated, and the alcohol product was purified by column chromatography (SiO_2, 10:1 *n*-hexane−ethyl acetate). 3-Methoxyphenyl isobutyl ketone (**15**): ^{1}H NMR ($CDCl_3$) δ 7.53 (d, J = 8 Hz, 1H, C*H* of Ph), 7.48 (s, 1H, C*H* of Ph), 7.37 (t, J = 8 Hz, 1H, C*H* of Ph), 7.10 (dd, J = 3 Hz, J = 8 Hz, 1H, C*H* of Ph), 3.86 (s, 3H, −OMe), 2.82 (d, J = 7 Hz, 2H, COC*H*$_2$), 2.30 (m, 1H, C*H*Me$_2$), 1.00 (d, J = 7 Hz, 6H, CH*Me*$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 200.1 (s, C=O), 159.8 (s), 138.8 (s), 129.5 (s), 120.8 (s), 119.3 (s), 112.3 (s), 55.4 (s), 47.6 (s), 25.2 (s), 22.8 (s). GC/MS data: 192 (M^+), 177 (M^+ − Me), 150, 135 (M^+ − CH_2CHMe_2), 107, 92, 77.

X-ray Crystallography. X-ray diffraction data were collected at 90 K on either a Nonius kappaCCD diffractometer (Mo Kα radiation for the structures of **7a** and **10**) or a Bruker-Nonius X8 Proteum diffractometer (Cu Kα for the structure of **2**) from crystals mounted in Paratone oil. Raw data were integrated, scaled, merged, and corrected for Lorentz−polarization effects using either the HKL-SMN package[35] (structures **7a** and **10**) or the APEX2 programs.[36] The structures were solved by direct methods (SHELXS97)[37] and difference Fourier methods (SHELXL97).[37] Refinement was carried out against F^2 by weighted full-matrix least squares (SHELXL97).[37] All nondisordered hydrogen atoms were found in difference maps and subsequently placed at calculated positions and refined using riding models with isotropic displacement parameters derived from their attached atoms (disordered hydrogens were simply calculated). Non-hydrogen atoms were refined with anisotropic displacement parameters using atomic scattering factors were taken from ref 38.

Acknowledgment. Support of this research by the NSF (Grant Nos. CHE-0517798 to O.V.O. and MRI-0319176 to S.P.), Alfred P. Sloan Foundation (Research Fellowship to O.V.O.), and Brandeis University is gratefully acknowledged.

Supporting Information Available: Text giving additional synthetic details, figures giving NMR spectra, and CIF files giving crystallographic data for **2**, **7a**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060464R

(35) Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Macromolecular Crystallography, A*; Carter, C. W., Jr., Sweet, R. M., Eds.; Methods in Enzymology 276; Academic Press: New York, 1997; pp 307−326.

(36) APEX2-Programs for Data Collection and Processing of X-ray Diffraction Data; Bruker-Nonius, Madison, WI, 2004.

(37) Sheldrick, G. M. SHELX97-Programs for Crystal Structure Solution and Refinement; University of Gottingen, Gottingen, Germany, 1997.

(38) *International Tables for Crystallography*; Hahn, T., Ed.; Kluwer Academic: Dordrecht, The Netherlands; Vol. C (Mathematical, Physical and Chemical Tables).