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Phosphine Loss from Bis(phosphine)rhodium(I) η^2-(C,O)-Diphenylketene Complexes Leading to η^4-(C_4) Coordination and Fluxionality of the Ketene

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Significant structural changes accompany phosphine loss from bis(phosphine) complexes *trans*-ClRh[η^2-(C,O)-$Ph_2C{=}C{=}O$](PR_3)$_2$ [**4**, where PR_3 = PMe(t-Bu)$_2$, P(i-Pr)$_3$, or PCy$_3$], giving ClRh[η^4-(C_4)-$Ph_2C{=}C{=}O$](PR_3) (**5**). As shown by the X-ray crystal structure of **5a** [PR_3 = PMe(t-Bu)$_2$] and variable-temperature NMR studies, the metal moves from the ketene C,O bond to the C,C bond and also coordinates weakly to two carbons of a ketene phenyl substituent, resulting in fluxional behavior unique among complexes of aryl- or vinyl-substituted ketenes.

Introduction

Metal−ketene complexes[1] have been proposed as intermediates in a number of important reactions, from industrial Fischer−Tropsch synthesis and reductions of CO_2[2] to thermal[3] and photochemical reactions of metal−carbene−CO complexes.[4] In many of these transformations, very little or nothing is known about the bonding of the metal to the ketene unit, because metal−ketene complexes are not detected.[5] In contrast, Grotjahn and Lo have reported a series of studies of iridium−ketene complexes featuring the same metal fragment, *trans*-[P(i-Pr$_3$)$_2$]IrCl, bound to the C,O bond of diphenylketene (**1**, Scheme 1) and to the C,C bond of phenylketene (**2**).[6] These complexes are sufficiently stable to be isolated and characterized, yet reactive in C−H bond activation[7] and C−C bond-forming processes.[8] In the latter case, spectroscopic evidence was given for a reactive iridium−ketene−alkyne complex (**3**) in which the metal is coordinated to diphenylketene in an η^4-(C_4) fashion through the C,C bond of the ketene unit and to one C,C bond of a phenyl substituent. Because of the further reactivity of these complexes, only characterization by NMR spectroscopy was possible.[8] Here for the first time X-ray crystallographic evidence for similar ketene coordination to Rh is presented. Significantly, a change in ketene coordination is seen when a series of three bis(phosphine)Rh η^2-(C,O)-ketene complexes **4** lose one phosphine, giving **5**. Products **5** are shown by NMR spectroscopy to feature a fluxional η^4-(C_4)-($Ph_2C{=}C{=}O$) ligand with weaker coordination of the phenyl carbons than of the ketene carbons, behavior unique among aryl- or vinyl-substituted ketene complexes with η^4-coordination.[9,10,11]

Results and Discussion

Syntheses. Using a procedure that we reported for the preparation of Ir bis(phosphine) complex **1**,[7] the

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† Corresponding author for crystal structure.

(1) (a) Geoffroy, G. L.; Bassler, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1−83. (b) For an especially good leading reference, see: Hofmann, P.; Perez-Moya, L. A.; Steigelmann, O.; Riede, J. *Organometallics* **1992**, *11*, 1167−1176, and references therein. (c) Reviews of ketene chemistry: Tidwell, T. T. *Acc. Chem. Res.* **1990**, *23*, 273−279. Tidwell, T. T. *Ketenes*; Wiley: New York, 1995.

(2) (a) Keim, W. *Catalysis in C1 Chemistry*; D. Reidel: Dordrecht, 1983. (b) Rofer-dePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447−474. (c) Hermann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117−130. (d) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121−127. (e) Blyholder, G.; Emmett, P. H. *J. Phys. Chem.* **1960**, *64*, 470−472. (f) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136−141.

(3) (a) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Chapter 5.3, pp 469−548. (b) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 1065−1113. (c) Dötz, K.-H. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer: Berlin, 1988. (d) Kim, O. K.; Wulff, W. D.; Jiang, W.; Ball, R. G. *J. Org. Chem.* **1993**, *58*, 5571−5573. (e) Harvey, D. F.; Grenzer, E. M.; Gantzel, P. K. *J. Am. Chem. Soc.* **1994**, *116*, 6719−6732.

(4) (a) Reviews: Schmalz, H.-G. *Nachr. Chem., Technol. Lab.* **1994**, *42*, 608−612. (b) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Chapter 5.4, pp 549−576. (c) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122−2126. (d) Merlic, C. A.; Xu, D.; Gladstone, B. G. *J. Org. Chem.* **1993**, *58*, 538−545.

(5) For an exception, see: Anderson, B. A.; Bao, J.; Brandvold, T. A.; Challener, C. A.; Wulff, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 10671−10687, and refs 27 and 28 therein.

(6) Grotjahn, D. B.; Lo, H. C. *Organometallics* **1995**, *14*, 5463−5465.

(7) Grotjahn, D. B.; Lo, H. C. *J. Am. Chem. Soc.* **1996**, *118*, 2097−2098.

(8) Lo, H. C.; Grotjahn, H. C. *J. Am. Chem. Soc.* **1997**, *119*, 2958−2959.

(9) Fe(CO)$_3$[η^4-(C_4)-$Ph_2C{=}C{=}O$] [**6**, 38% yield from Fe(CO)$_5$ and $Ph_2C{=}C{=}O$] is the only other arylketene complex with a metal coordinated to both the ketene unit and an aryl group; it did not show fluxionality of the ketene ligand. Bkouche-Waksman, I.; Ricci, J. S., Jr.; Koetzle, T. F.; Weichmann, J.; Herrmann, W. A. *Inorg. Chem.* **1985**, *24*, 1492−1499. Herrmann, W. A.; Gimeno, J.; Weichmann, J.; Ziegler, M.; Balbach, M. *J. Organomet. Chem.* **1981**, *213*, C26−C30.

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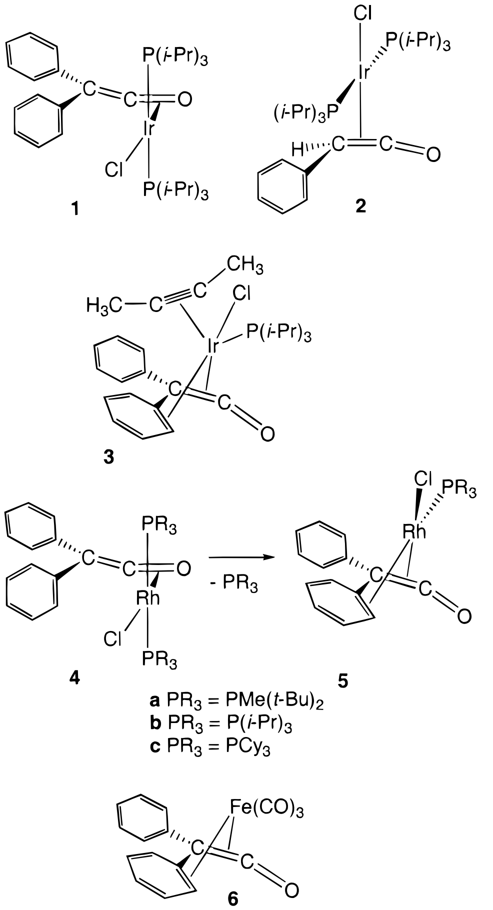
Scheme 1



three Rh bis(phosphine) complexes of diphenylketene (**4**) were prepared[12] in near-quantitative yields by combination of diphenylketene, 2 mol of hindered phosphine PMe(*t*-Bu)$_2$ (**a**), P(*i*-Pr)$_3$ (**b**), or PCy$_3$ (**c**), and 0.5 mol of the Rh(I) dimer [Rh(cyclooctene)$_2$(μ-Cl)]$_2$.[13] In **4**, the coordination of the ketene through the C,O bond is clear from comparison of the spectral data with those of crystallographically characterized **1**[6] and **4b**.[12b]

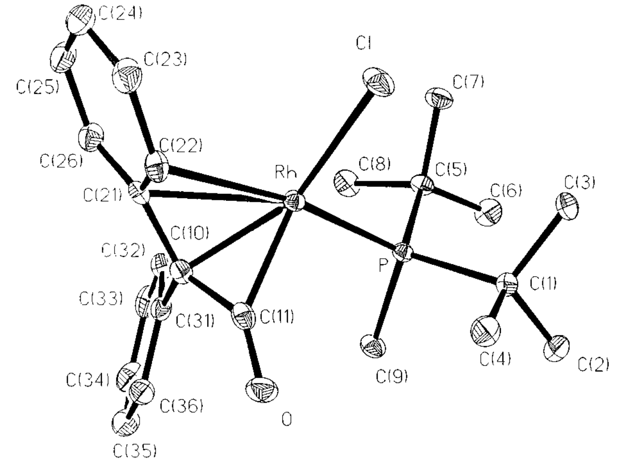


Figure 1. Molecular structure of **5a**.

Although the Rh complexes **4** are stable in benzene solution for days at room temperature, in the presence of [Rh(cyclooctene)$_2$(μ-Cl)]$_2$ or CuI over 1−3 days they give monophosphine complexes **5**, the rate of the reaction being fastest for **4a** and slowest for **4c**. A more efficient synthesis of **5** started with only 1.5 mol of hindered phosphine PR$_3$, 1 mol of diphenylketene, and 0.5 mol of the Rh(I) dimer [Rh(cyclooctene)$_2$(μ-Cl)]$_2$ in C$_6$D$_6$ for 1 day. Use of less than 1.5 mol of phosphine led to lower yields. Under these conditions, according to integration of ^{1}H NMR spectra of solutions, PMe(*t*-Bu)$_2$-derived complexes **5a** and **4a** were present in a ratio of 4:1. After adding CuI (5 equiv) to trap released phosphine and waiting for 1 day, the ratio of **5a** to **4a** increased to 20:1, and chromatography over silica afforded monophosphine complex **5a** in 89% yield. The phosphine-trapping step could be accelerated using CuCl (5 equiv), which completed the formation of **5a** within 7 h. The reaction of P(*i*-Pr)$_3$, diphenylketene, and [Rh(cyclooctene)$_2$(μ-Cl)]$_2$ for 1 day produced a mixture containing **5b** and **4b** in a ratio of 6:1. After treatment with CuI for 1 day, no **4b** was detected, and **5b** was isolated in 71% yield. Finally, after allowing PCy$_3$, diphenylketene, and [Rh(cyclooctene)$_2$(μ-Cl)]$_2$ to react for 1 day, the ratio of **5c** and **4c** was 1:1, which after 1 and 3 days of exposure to CuI increased to 3.4:1 and 9:1, respectively. Subsequent chromatography afforded **5c** in 50% yield. As in the case of the PMe(*t*-Bu)$_2$ analogue, the use of CuCl speeded the phosphine trapping step, allowing purification of **5c** after only 1 day and improving the yield to 65%.

Structure of 5a. The three-dimensional structure of **5a** was revealed by X-ray diffraction of a suitable crystal (Figure 1). Table 1 lists details of the crystal used, data collection, and solution and refinement. Selected bond distances and angles are given in Table 2. The η^4-(C_4) bonding of the diphenylketene ligand is quite unsymmetrical. The bond distance between Rh and the ketene C=O carbon is the shortest [1.933(4) Å], followed by the distance to the other ketene carbon C=C=O [2.140(4) Å], and then the distances to the phenyl quaternary and CH carbons [2.338(4) and 2.412(4) Å, respectively]. Comparison of these data with those for the five other crystallographically characterized η^2-(C,C)-ketene com-

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[10] η^4-(C_4)-Vinylketene complexes characterized by X-ray diffraction: (a) Binger, P.; Ĉetinkaya, B.; Krüger, C. *J. Organomet. Chem.* **1978**, *159*, 63−72. (b) Newton, M. G.; Pantaleo, N. S.; King, R. B.; Chu, C.-K. *J. Chem. Soc., Chem. Commun.* **1979**, 10−12. (c) Jens, K. J.; Weiss, E. *Chem. Ber.* **1984**, *117*, 2469−2478. (d) Templeton, J. L.; Herrick, R. S.; Rusik, C. A.; McKenna, C. E.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1985**, *24*, 1383−1388. (e) Wulff, W. D.; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520−522. (f) Mayr, A.; Asaro, M. F.; Glines, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2215−2216. (g) Valéri, F.; Meier, F.; Weiss, E. *Chem. Ber.* **1988**, *121*, 1093−1100. (h) Mitsudo, T.; Watanabe, H.; Sasaki, T.; Takegami, Y.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Organometallics* **1989**, *8*, 368−378. (i) Alcock, N. W.; Richards, C. J.; Thomas, S. E. *Organometallics* **1991**, *10*, 231−238. Complexes with additional coordination to an amino substituent: (j) Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 8615−8617. (k) Chelain, E.; Parlier, A.; Rudler, H.; Daran, J. C.; Vaissermann, J. *J. Organomet. Chem.* **1991**, *419*, C5−C9.

[11] η^2-(C,C)-Ketene complexes characterized by X-ray diffraction: (a) Herrmann, W. A.; Redhouse, A. D. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 615−616. (b) Herrmann, W. A.; Plank, J.; Ziegler, M.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133−3135. (c) Herrmann, W. A.; Plank, J.; Kriechbaum, G. W.; Ziegler, M. L.; Pfisterer, H.; Atwood, J. L.; Rogers, R. D. *J. Organomet. Chem.* **1984**, *264*, 327−352. (d) Grotjahn, D. B.; Lo, H. C.; Hubbard, J. L. Unpublished results.

[12] (a) Full details will appear in: Grotjahn, D. B.; Wolpert, M.; Lo, H. C.; Bikzhanova, G.; Hubbard, J. L. Manuscript to be submitted to *J. Am. Chem. Soc.* (b) While this work was in progress, the preparation and molecular structure of **4b** appeared in: Bleuel, E.; Laubender, M.; Weberndörfer, B.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 156−159.

[13] van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92−95.

Table 1. Crystal Data and Structure Refinment for 5a

empirical formula	$C_{23}H_{30}ClOPRh$
color	orange
cryst size (mm)	0.15 × 0.2 × 0.4
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	$a = 11.315(3)$ Å $b = 8.720(3)$ Å $c = 23.312(6)$ Å $\beta = 99.60(2)°$
volume	2267.9(10) Å^3
Z	4
fw	491.8
density (calc)	1.440 Mg/m^3
absorp coeff	0.939 mm^{-1}
F(000)	1012
diffractometer used	Siemens P4
radiation	Mo Kα ($\lambda = 0.71073$ Å)
temp (K)	173
monochromator	highly oriented graphite crystal
2*θ* range	3.6−50.0°
scan type	$2\theta-\theta$
scan speed	variable; 3.00−14.65 deg/min in *x*
scan range (*x*)	0.50° plus Kα-separation
background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
standard reflns	1 measured every 50 reflns
index ranges	$-13 \leq h \leq 0, 0 \leq k \leq 10$ $0 \leq l \leq 27$
no. of reflns collected	4546
no. of indep reflns	4018 ($R_{int} = 2.95\%$)
no. of obsd reflns	3168 ($F > 4.0\sigma(F)$)
absorp corr	N/A
system used	Siemens SHELXTL PLUS (VMS)
solution	direct methods
refinement method	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
hydrogen atoms	riding model, fixed isotropic *U*
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0009F^2$
no. of params refined	244
final *R* indices (obs data)	$R = 3.08\%$, $R_w = 4.16\%$
R indices (all data)	$R = 4.55\%$, $R_w = 4.58\%$
goodness-of-fit	1.03
largest and mean *D*/*r*	0.001, 0.000
data-to-parameter ratio	13.0:1
largest difference peak	0.53 e Å^{-3}
largest difference hole	−0.34 e Å^{-3}

Table 2. Selected Bond Distances (Å) and Angles (deg) for 5a

Rh−C(11)	1.933(4)	C(23)−C(24)	1.380(7)
Rh−C(10)	2.140(4)	C(24)−C(25)	1.412(7)
Rh−C(21)	2.338(4)	C(25)−C(26)	1.351(6)
Rh−C(22)	2.412(4)	C(21)−C(26)	1.407(6)
Rh−Cl	2.350(1)	Cl−Rh−P	96.4(1)
Rh−P	2.285(1)	Rh−C(11)−O	140.1(3)
C(11)−O	1.194(5)	O−C(11)−C(10)	142.3(4)
C(10)−C(11)	1.442(6)	Rh−C(11)−C(10)	77.2(2)
C(10)−C(21)	1.476(5)	C(10)−C(21)−C(22)	117.7(3)
C(21)−C(22)	1.411(6)	C(10)−C(21)−C(26)	123.5(3)
C(22)−C(23)	1.407(5)	C(22)−C(21)−C(26)	118.5(3)

plexes[11] indicates that **5a** is essentially an η^2-(*C*,*C*)-ketene complex with an additional very weakly bound olefinic ligand. If the ketene carbons are numbered C(2)═C(1)═O, in the other known structures, M−C(2), M−C(1), and C(2)−C(1) distances exhibit ranges of 2.140−2.242, 1.935−1.976, and 1.35−1.468 Å, respectively, whereas the same data for **5a** are very similar (2.140, 1.933, and 1.442 Å, respectively). However, complex **5a** is distinctly different than the one other known η^4-(C_4)-$Ph_2C{=}C{=}O$ complex (**6**),[9] for which a high-precision neutron diffraction structure exists. The iron complex was described as an η^1-acyl-η^3-allyl species,[9] because the three bonds from Fe to ketene C(2) and the two phenyl carbons were all very similar in length [2.133(2), 2.177(2), 2.260(2) Å, respectively]. Known structures of *vinyl*ketene complexes show the same trend.[10] In contrast, in **5a** the phenyl quaternary carbon is 0.20 Å more distant from the metal than ketene C(2), and the phenyl CH carbon is even further removed (0.27 Å).

Spectroscopic Characterization and Ligand Binding. Significantly, Rh complexes **5** feature a fluxional diphenylketene ligand, whereas the Fe analogue **6**[9] and known vinylketene complexes[10] do not. Solution-phase NMR studies on **5** suggest movement of the coordinated phenyl ring in each complex. At 500 MHz and 30 °C in C_6D_6 or CD_2Cl_2, **5** showed a broad two-proton resonance near 7 ppm. For **5a** in CD_2Cl_2 (Figure 2), as the temperature was lowered to 20 °C, the resonance near 7.0 ppm broadened considerably, decoalesced near 0 °C, and at −50 °C appeared as two relatively sharp doublets at 6.11 and 7.96 ppm, ascribed to the phenyl protons ortho to the ketene unit. The upfield proton resonance is assigned to the coordinated portion of the phenyl ring, in analogy with the upfield chemical shifts seen for carbons and protons of the bound portion of other η^2-arene complexes.[14] Using COSY and HMQC data,[15] the associated carbons ortho to the ketene moiety were assigned to resonances at δ 98.20 (dd, $J = 26.0$ and 11.0 Hz, coordinated carbon) and 123.19 ppm (d, $J = 21.0$ Hz, uncoordinated carbon). Similarly, for the phenyl protons meta to the ketene unit, on going from 20 to −50 °C, a two-proton triplet at 7.65 ppm was replaced by two one-proton triplets at 7.63 and 7.69 ppm.

From these data, $\Delta G^\ddagger$ for the movement of the phenyl ring must be on the order of 12 kcal mol^{-1}. The spectroscopic behavior of **5a** is consistent with movement of the metal from one side of the phenyl ring to the other, a process characterized in some other η^2-arene complexes.[14e−g]

Using gradient COSY, HMQC, and HMBC data on **5a** both in CD_2Cl_2 at −50 °C and in C_6D_6 at 30 °C, most of the proton and carbon resonances could be assigned, particularly in the coordinated phenyl ring.[15] Figure 3 shows the assignments that could be made with cer-

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(14) Leading references: (a) Chordia, M. D.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 5637−5642. (b) Winemiller, M. D.; Kelsch, B. A.; Sabat, M.; Harman, W. D. *Organometallics* **1997**, *16*, 3672−3678. (c) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725−5731. (d) Tagge, C. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 6908−6915. (e) Conry, R. R.; Striejewske, W. S.; Tipton A. A. *Inorg. Chem.* **1999**, *38*, 2833−2843. (f) Li, C.-S.; Jou, C.-H.; Jou, D.-C. *Organometallics* **1993**, *12*, 3945−3954. (g) Li, C.-S.; Cheng, C.-H.; Liao, F.-L.; Wang, S.-L. *J. Chem. Soc., Chem. Commun.* **1991**, 710−713. (h) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91−100. (i) Benn, R.; Mynott, R.; Topalović, I.; Scott, F. *Organometallics* **1989**, *8*, 2299−2305. (j) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305−306. (k) van der Heijden, H.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576−1578.

(15) Selected NMR spectra for **5a**−**c** appear in the Supporting Information. Overlapping resonances in either solvent prevented full assignments. Several aromatic ring carbons appeared near δ 128−129 ppm, and it was not possible to assign these peaks unequivocally. Moreover, whereas for **5a** in C_6D_6 at 30 °C, the two resonances for the methyl carbons of the diastereotopic *t*-Bu groups appeared as readily identifiable doublets, in CD_2Cl_2 at −50 °C (the temperature required obtaining reasonably sharp peaks in ^{1}H NMR spectra for the ortho protons of the coordinated phenyl ring), the signals for the methyl carbons appeared as a more complex pattern, perhaps because of hindered rotation of the *t*-Bu groups.

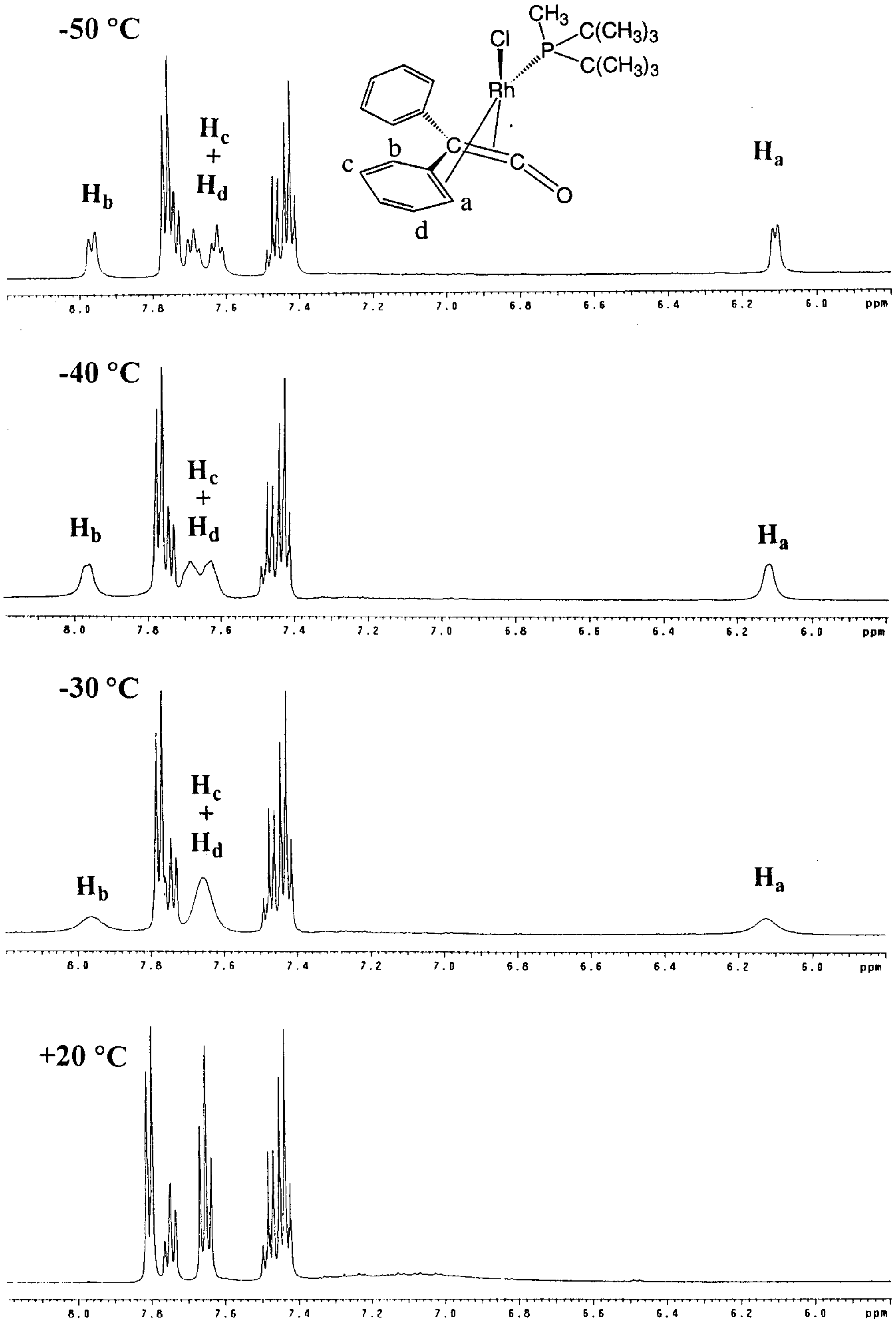

Figure 2. ^{1}H NMR spectrum of **5a** (CD_2Cl_2, 500 MHz) at various temperatures.

tainty at low temperature; the presence of COSY cross-peaks between the upfield resonance at δ 6.11 ppm (ortho hydrogen of coordinated portion of the phenyl ring) and the triplet at 7.63 identified the latter as the absorbance of the nearby meta proton. The associated carbon at the meta position (identified by HMQC) resonated at 136.53 ppm and appeared as a doublet with a considerable coupling (34.4 Hz). Similarly, starting with the readily identifiable absorbance at δ 7.96 ppm for the ortho proton of the uncomplexed part of the coordinated phenyl ring, the resonances for the other meta proton (7.69 ppm) and the carbon to which it was attached (134.0 ppm, d, $J = 34.4$ Hz) could be identified. Although the flipping of the coordinated phenyl ring was not investigated by ^{13}C NMR, it is notable that in the $^{13}C\{^1H\}$ NMR spectrum of **5a** at 30 °C in C_6D_6 there is a single somewhat broadened singlet at 136.05 ppm, which we ascribe as the averaged signal for the two meta carbons. In confirmation of this, for a sample at 30 °C in C_6D_6 there is an HMQC cross-peak between the carbon resonance at 136.05 and a slightly broadened two-proton triplet at 7.28 ppm, which is attributed to

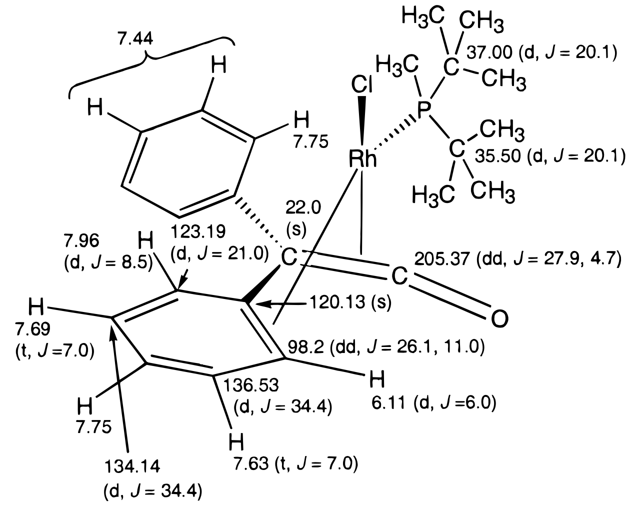

Figure 3. Assignment of NMR resonances for **5a** (CD_2Cl_2, −50 °C, 500 MHz) that could be made with certainty. Chemical shifts are in ppm and coupling constants in Hz.

the meta protons. Similarly, in the $^{13}C\{^1H\}$ NMR spectra of **5a** and **5b** at 30 °C in C_6D_6, a broad resonance near δ 111 ppm could be described as the averaged absorption of the ortho carbons of the coordinated phenyl ring.

For **5a** at −50 °C, using HMBC data, the singlet at 120.13 ppm could be assigned to the ipso carbon of the coordinated phenyl ring. Finally, the resonances for the carbons of the ketene unit C(2)═C(1)═O were identified as the singlet at 22.00 and the doublet of doublets ($J =$ 27.9 and 4.7 Hz) at 205.37 ppm, respectively. Although ^{13}C NMR shifts do not appear to be an especially reliable means of determining whether a metal is coordinated to the C,C or C,O bond of a ketene,[16] in comparison, the data for C(2) and C(1) in the η^2-(*C*,*C*)-phenylketene complex **2** (isolated[6]) and η^4-(C_4)-diphenylketene complex **3** (characterized in situ[8]) are −33.03 and 198.18 ppm for **2** and 55.03 and 204.87 ppm for **3**.

For **5a**−**c**, IR absorptions in the range 1801−1804 cm^{-1} are in accord with data for known η^4-vinylketene complexes.[10] Meanwhile, in the series of complexes **5a**−**c**, $^{31}P\{^1H\}$ NMR data are similar, δ 56.10−65.64 ppm (d, $^1J_{RhP} = 218.9-228.0$ Hz). In early stages of reactions used to make **5a**−**c**, in $^{31}P\{^1H\}$ NMR spectra a doublet of similar chemical shift and coupling constant was observed, suggesting the presence of an intermediate, presumed to be the diastereomer of **5** in which the chloride and phosphine ligands are switched.

Finally, the relatively weak coordination of the phenyl substituent manifested itself in facile ligand addition: within 1 h at room temperature, monophosphine complexes **5** add phosphine PR_3, to give the bis(phosphine) complexes **4** in quantitative yields, suggesting that a rich ligand substitution chemistry on **5** remains to be explored.

Conclusions

In summary, significant structural changes accompany phosphine loss from bis(phosphine) complexes **4**: the metal moves from the ketene C,O bond to the C,C bond, to which the metal is bound most tightly in **5**. In addition, in **5** relatively weak coordination of a ketene phenyl substituent is seen. These structural features confirm an earlier proposal for a related Ir complex.[8] The structure and reactivity of the new Rh complexes toward ligands is the subject of ongoing investigations, results that will contribute to our fundamental understanding of the interactions of ketenes and late transition metals.

Experimental Section

General Experimental. Reactions were performed in resealable NMR tubes (J. Young or Wilmad Glass) under nitrogen, using a combination of Schlenk line and glovebox techniques. C_6D_6 was distilled from $LiAlH_4$. Radial chromatography was carried out with a Harrison Research Chromatotron under N_2 atmosphere; silica gel (SiO_2) and deoxygenated solvents were used.

Unless otherwise specified, ^1H, ^{13}C, and ^{31}P data were measured at 30 °C on a 200 MHz (50.3 MHz for ^{13}C and 80 MHz for ^{31}P) or nominal 500 MHz (499.9 MHz for ^1H, 125.7 MHz for ^{13}C) spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to residual solvent resonances (^1H NMR, 7.15 for $C_6\mathit{H}D_5$ and 5.28 for $C\mathit{H}DCl_2$; ^{13}C NMR, 128.39 for C_6D_6 and 53.98 for CD_2Cl_2), where ^1H NMR chemical shifts are followed by multiplicity, coupling constants *J* in hertz, and integration in parentheses. For complex coupling patterns (e.g., dt, $J =$ 3.2, 7.6 Hz, 1 H), multiplicities and coupling constants are listed in the same order; for example, the doublet (d) is characterized by the smaller coupling, and the triplet (t) by the larger coupling. The abbreviations “br” and “sl br” designate broad and slightly broad signals, respectively. $^{31}P\{^1H\}$ NMR chemical shifts are referenced to external 85% H_3PO_4 (aq).

IR spectra were obtained on a Perkin-Elmer-1600 FTIR spectrometer. Samples were examined in C_6D_6 solutions in NaCl cells. Elemental analyses were performed at NuMega Resonance Labs, San Diego, CA.

Synthesis of 5, Represented by the Procedure for 5a {ClRh(η^4-C_4-Ph_2C═C═O)[PMe(*t*-Bu)$_2$]}. A resealable NMR tube was charged with [Rh(cyclooctene)$_2$(μ-Cl)]$_2$ (109 mg, 0.152 mmol) and $[(CH_3)_3Si]_4C$ (3.6 mg, 0.01 mmol, internal standard) in a nitrogen-filled glovebox, and C_6D_6 (~0.7 mL) was added to give a suspension. To this was added Ph_2C═C═O (60.0 mg, 0.309 mmol) via syringe, followed by PMe(*t*-Bu)$_2$ (75.2 mg, 0.469 mmol). Upon the addition of the phosphine, a clear yellowish red solution was formed. The tube was sealed and shaken to mix the contents well before removal from the glovebox, and the tube was kept at room temperature, protected from light with aluminum foil. The reaction was followed by ^1H and $^{31}P\{^1H\}$ NMR spectra and was considered to be complete after 24 h, when there was no detectable [Rh(cyclooctene)$_2$(μ-Cl)]$_2$. The NMR tube was opened in the glovebox, and CuI (143 mg, 0.751 mmol) was added. TLC analysis of the final reaction mixture was conducted in the glovebox, and the reaction mixture was then subjected to radial chromatography (Chromatotron, 2 mm SiO_2 plate, gradient elution starting with petroleum ether/ethyl acetate = 10:1) to yield a small amount of **4a** as a red solid, followed by **5a** (131.0 mg, 89%) as an orange solid. Using CuCl instead of CuI reduced the time required for consumption of **4a** to 7 h, while giving a similar yield of **5a**: IR (C_6D_6, NaCl) 1801 cm^{-1}. Anal. Calcd for $C_{23}H_{31}ClRhOP$ (492.92): C, 56.04; H, 6.35. Found: C, 56.42; H, 6.75. Data at low temperature: ^1H NMR (CD_2Cl_2, 500 MHz, −50 °C) δ 7.96 (d, $J = 8.5$ Hz, 1 H, ortho proton of unbound portion of coordinated phenyl ring), 7.75 (m, 3 H), 7.69 (t, $J = 7.0$ Hz, 1 H), 7.63 (t, $J = 7.0$ Hz, 1 H), 7.44 (m, 3

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[16] η^2-(*C*,*C*)-bound ketene complexes exhibit chemical shifts for C(1) and C(2) in the ranges 166.8 to 255.7 and −33.0 to 74.7 ppm, respectively.[1a,6]

H), 6.11 (d, $J = 6.0$ Hz, 1 H, ortho proton of bound portion of coordinated phenyl ring), 1.42 [d, $J = 14.0$ Hz, 9 H, $\mathrm{PC(C}H_3)_3$], 0.97 [d, $J = 14.0$ Hz, 9 H, $\mathrm{PC(C}H_3)_3$], 0.55 ppm (d, $J = 8.0$ Hz, 3 H, $\mathrm{PC}H_3$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ ($\mathrm{CD_2Cl_2}$, 125 MHz, −50 °C) δ 205.37 (dd, $J = 27.9$, 4.7 Hz, $\mathrm{C{=}}C\mathrm{{=}O}$), 136.53 (sl br d, $J = 34.4$ Hz, meta carbon of coordinated ring), 134.14 (sl br d, $J = 34.4$ Hz, meta carbon of coordinated ring), 130.88 (d, $J = 28.5$ Hz, ortho carbons of uncoordinated ring), 130.00 (s), 128.90 (d, $J = 11.6$ Hz), 128.57 (s), 128.30 (d, $J = 15.5$ Hz), 123.19 (d, $J = 21.0$ Hz, unbound ortho carbon of coordinated ring), 120.13 (s, ipso carbon of coordinated ring), 98.20 (dd, $J = 26.1$, 11.0 Hz, ortho carbon bound to Rh), 37.00 (d, $J = 20.1$ Hz, $\mathrm{P}C\mathrm{Me_3}$), 35.50 (d, $J = 20.1$ Hz, $\mathrm{P}C\mathrm{Me_3}$), 28.6−29.9 [m, $\mathrm{PC(}C\mathrm{H_3)_3}$], 22.00 (s, $C\mathrm{{=}C{=}O}$), 4.64 ppm (d, $J = 27.0$ Hz, $\mathrm{P}C\mathrm{H_3}$). Assignments for the signals at 128.90, 128.57, and 128.30 ppm are tentative.[15] Data at ambient temperature: ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C, 500 MHz) δ 7.80 (dd, $J = 6.5$, 2.0 Hz, 2 H, ortho protons of uncoordinated phenyl ring), 7.28 (sl br t, $J \approx 7$ Hz, 2 H, meta protons of coordinated phenyl ring), 7.23 (dt, $J = 1$, 7.5 Hz, 1 H, para proton of coordinated phenyl ring), 7.07−7.12 (m, 3 H), 6.95 (br s, 2 H, ortho protons of coordinated phenyl ring), 1.49 [d, $J = 14.0$ Hz, 9 H, $\mathrm{PC(C}H_3)_3$] 0.88 [d, $J = 13.5$ Hz, 9 H, $\mathrm{PC(C}H_3)_3$], 0.51 ppm (dd, $J = 8.5$, 2.0 Hz, 3 H, $\mathrm{PC}H_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ ($\mathrm{C_6D_6}$, 30 °C, 81 MHz) 59.53 ppm (d, $J = 228.0$ Hz); $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{C_6D_6}$, 30 °C, 50.3 MHz) 205.46 (dd, $J = 23.1$, 4.2 Hz, $\mathrm{C{=}}C\mathrm{{=}O}$), 136.05 (s, meta carbons of coordinated phenyl ring), 132.07 (s), 131.64 (s), 129.23 (s), 128.18 (s), 121.47 (d, $J = 2.7$ Hz), 111 (br s, ortho carbons of coordinated phenyl ring), 37.84 (dd, $J = 20.1$, 1.4 Hz, $\mathrm{P}C\mathrm{Me_3}$), 35.82 (dd, $J = 19.6$, 1.5 Hz, $\mathrm{P}C\mathrm{Me_3}$), 30.19 [d, $J = 3.0$ Hz, $\mathrm{PC(}C\mathrm{H_3)_3}$], 29.79 [d, $J = 4.2$ Hz, $\mathrm{PC(}C\mathrm{H_3)_3}$], 23.02 (t, $J = 3.1$ Hz, $C\mathrm{{=}C{=}O}$), 5.53 ppm (dd, $J = 25.2$, 2.0 Hz, $\mathrm{P}C\mathrm{H_3}$). Observation of the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum at 125.7 MHz confirmed the identities of the doublets indicated. At the higher field strength, the resonance at 136.05 (ascribed to the meta carbons of the coordinated ring) was broader and that at 111 ppm (ortho carbons of coordinated ring) was not seen.

Compound 5b $\{\mathrm{ClRh}(\eta^4\text{-}C_4\text{-}\mathrm{Ph_2C{=}C{=}O})[\mathrm{P}(i\text{-}\mathrm{Pr})_3]\}$. In a fashion similar to that used for **5a**, $[\mathrm{Rh(cyclooctene)_2}(\mu\text{-}\mathrm{Cl})]_2$ (110 mg, 0.153 mmol), $\mathrm{Ph_2C{=}C{=}O}$ (58 mg, 0.30 mmol), $\mathrm{P}(i\text{-}\mathrm{Pr})_3$ (74 mg, 0.462 mmol), and CuI (142 mg, 0.746 mmol) were used to make **5b** as an orange solid (104.9 mg, 71%): ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C, 500 MHz) δ 7.79−7.81 (m, 2 H), 7.30 (sl br t, $J \approx 7.5$ Hz, 2 H), 7.23 (sl br t, $J \approx 7.5$ Hz, 1 H), 7.06−7.10 (m, 3 H), 6.91 (br s, 2 H), 2.14 (m, 3 H), 1.05 (dd, $J = 14.5$, 7.0 Hz, 9 H), 0.99 ppm (dd, $J = 14.5$, 7.0 Hz, 9 H); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 30 °C, 81 MHz) 65.64 ppm (d, $J = 220.2$ Hz); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 30 °C, 50.3 MHz), δ 204.65 (dd, $J = 23.3$, 4.1 Hz, $\mathrm{C{=}}C\mathrm{{=}O}$), 135.89 (sl br s, meta carbons of coordinated phenyl ring), 132.45 (s), 132.05 (s), 131.67 (s), 129.14 (s), 128.19 (s), 120.05 (d, $J = 3.1$ Hz), 111 (br s, ortho carbons of coordinated phenyl ring), 26.80 (dd, $J = 23.1$, 1.5 Hz, 3 C, $\mathrm{P}C\mathrm{HMe_2}$), 20.36 (s, 3 C), 20.05 (s, 3 C), 13.61 ppm (s, $C\mathrm{{=}C{=}O}$). Anal. Calcd for $\mathrm{C_{23}H_{31}ClRhOP}$ (492.92): C, 56.04; H, 6.35. Found: C, 55.74; H, 6.41. IR ($\mathrm{C_6D_6}$, NaCl): 1804 cm^{-1}.

Compound 5c $[\mathrm{ClRh}(\eta^4\text{-}C_4\text{-}\mathrm{Ph_2C{=}C{=}O})(\mathrm{PCy_3})]$. In a fashion similar to that used for **5a**, $[\mathrm{Rh(cyclooctene)_2}(\mu\text{-}\mathrm{Cl})]_2$ (111 mg, 0.155 mmol), $\mathrm{Ph_2C{=}C{=}O}$ (59 mg, 0.304 mmol), and $\mathrm{PCy_3}$ (128 mg, 0.456 mmol) were allowed to react for 1 day before CuI (144 mg, 0.756 mmol) was added, and the mixture was monitored by NMR spectroscopy. After 3 days, chromatography afforded **5c** as an orange solid (92.0 mg, 50%). Using CuCl instead of CuI reduced the time required to consume all of **4c** to 1 day and increased the yield of **5c** to 65%: ^{1}H ($\mathrm{C_6D_6}$, 30 °C, 500 MHz) δ 7.86 (dd, $J = 7.5$, 2.0 Hz, 2 H), 7.30 (br t, $J \approx 6$ Hz, 2 H), 7.19 (t, $J = 7.5$ Hz, 1 H), 7.11 (m, 3 H), 6.95 (br s, 2 H), 2.06−2.14 (m, 6 H), 1.95 (br d, $J \sim 10$ Hz, 3 H), 1.46−1.62 (m, 15 H), 0.91−1.01 (m, 9 H); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ ($\mathrm{C_6D_6}$, 30 °C, 81 MHz) δ 56.10 ppm (d, $J = 218.9$ Hz); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ ($\mathrm{C_6D_6}$, 30 °C, 50.3 MHz) δ 204.60 (dd, $J = 23.4$, 4.4 Hz, $\mathrm{C{=}}C\mathrm{{=}O}$), 135.96 (sl br s, meta carbons of coordinated phenyl ring), 132.50 (s), 131.96 (s), 129.29 (s), 128.15 (s), 120.52 (d, $J = 3.5$ Hz), 36.85 (dd, $J = 23.6$, 1.8 Hz, 3 C), 31.15 (s, 3 C), 30.26 (s, 3 C), 28.27 (d, $J = 12.4$ Hz, 3 C), 27.81 (d, $J = 10.7$ Hz, 3 C), 26.64 (d, $J = 1.2$ Hz, 3 C), 15.79 ppm (s, $C\mathrm{{=}C{=}O}$). Both the broad peak for the ortho carbons of the coordinated phenyl ring (expected to be near 111 ppm) and another peak were missing. Anal. Calcd for $\mathrm{C_{32}H_{43}ClRhOP}$ (613.13): C, 62.68; H, 7.08. Found: C, 62.45; H, 7.10. IR ($\mathrm{C_6D_6}$, NaCl): 1803 cm^{-1}.

X-ray Structure of 5a. A suitable specimen was mounted vertically in an X-ray capillary tube and positioned in a goniometer head. The head was then attached to a Siemens P4 autodiffractometer precooled to −100 °C with the LT-2a low-temperature device. The Siemens random search program located 25 reflections between 15° and 30° 2θ. Centering these reflections indicated a monoclinic primitive cell. Collection was conducted on half of the hemisphere. Data reduction gave the unambiguous $P2/1c$ space group (No. 14). Direct methods successfully located the Rh, Cl, and P atoms and most of the other non-hydrogen atoms. The remaining non-hydrogen atoms were located by successive least-squares cycles. Hydrogen atoms were assigned riding on the carbon atoms. The Siemens package of programs (P3, SHELXS, SHELXL) was used exclusively for the structure determination and refinement.

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Supporting Information Available: Complete details of the X-ray diffraction study on **5a** and NMR spectra of **5a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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