An Unprecedented Type of Insertion of an Alkyne into a Metal−Carbon Bond

Kerstin Ilg and Helmut Werner*

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Received October 22, 1999

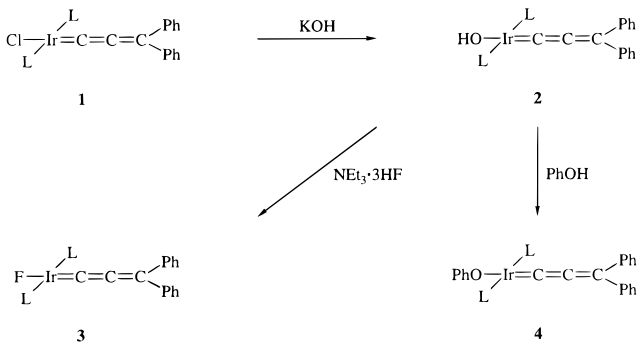
*Summary: Treatment of the (allenylidene)iridium complex trans-[IrCl(=C=C=CPh$_2$)(PiPr$_3$)$_2$] (**1**) with KOH leads to trans-[Ir(OH)(=C=C=CPh$_2$)(PiPr$_3$)$_2$] (**2**), which reacts with Brønsted acids such as HF and phenol to give trans-[IrF(=C=C=CPh$_2$)(PiPr$_3$)$_2$] (**3**) and trans-[Ir(OPh)(=C=C=CPh$_2$)(PiPr$_3$)$_2$] (**4**). Moreover, an unusual reaction of **2** with excess alkynes RC≡CH (R = Ph, CO$_2$Me) takes place to afford trans-[Ir(C≡CR)$_2$\{(E)-CH=CRCH=C=CPh$_2$\}(PiPr$_3$)$_2$] (**5**, **6**). Compounds **3** and **5** were characterized by X-ray structure analysis.*

In a continuation of our studies to prepare highly reactive rhodium−allenylidenes of the general composition *trans*-[Rh(X)(=C=C=CRR′)(P*i*Pr$_3$)$_2$],[1] we recently reported that the hydroxo derivatives (X = OH) react with acetic acid and phenol at room temperature to give the corresponding acetato (X = MeCO$_2$) and phenolato (X = OPh) metal compounds in excellent yield.[2] Moreover, these square-planar (allenylidene)rhodium(I) complexes undergo in the presence of CO a migratory insertion of the C=C=CRR′ unit into the Rh−O bond to generate γ-functionalized alkynyl ligands.[2,3] Following this work, we have now prepared the hydroxoiridium(I) compound **2**, which seems to be an even more promising starting material than the rhodium counterpart for carrying out substitution and insertion reactions.

Treatment of the chloro derivative **1**[4] in acetone with an excess of KOH results in a clean and nearly quantitative formation of the hydroxo complex **2** (Scheme 1).[5] The presence of the hydroxo ligand is indicated both by the strong absorption at 3643 cm^{-1} in the IR and by the broadened singlet at δ 4.25 in the ^{1}H NMR spectrum.[6]

Like the hydroxorhodium derivatives *trans*-[Rh(OH)(=C=C=CRR′)(P*i*Pr$_3$)$_2$],[1] compound **2** reacts with equimolar amounts of Brønsted acids such as HF (used as the adduct NEt$_3$·3HF)[7] and phenol to afford the substitution products **3** and **4** in, respectively, 88% and 82% yields.[8,9]

Scheme 1[a]



1 **2** **3** **4**

[a] L = P*i*Pr$_3$.

(1) Werner, H. *Chem. Commun.* **1997**, 903−910.

(2) Werner, H.; Wiedemann, R.; Laubender, M.; Wolf, J.; Windmüller, B. *Chem. Commun.* **1996**, 1413−1414.

(3) Laubender, M. Ph.D. Thesis, Universität Würzburg, Germany, 1998.

(4) Werner, H.; Lass, R. W.; Gevert, O.; Wolf, J. *Organometallics* **1997**, *16*, 4077−4088.

(5) The preparation of **2** is as follows. A solution of **1** (70 mg, 0.09 mmol) in 20 mL of acetone was treated with KOH (34 mg, 0.60 mmol), and the mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo, the residue was suspended in 50 mL of pentane, and the solution was filtered. The filtrate was concentrated to 3 mL in vacuo and stored at −78 °C in order to complete crystallization. The orange solid was separated from the mother liquor, washed with small quantities of pentane, and dried: yield 54 mg (84%); mp 104 °C dec. Anal. Calcd for C$_{33}$H$_{53}$IrOP$_2$: C, 55.05; H, 7.42. Found: C, 55.53; H, 7.57.

(6) Selected spectroscopic data for **2**−**5**, with the ^{1}H and ^{13}C NMR data for the aryl groups omitted, are as follows (abbreviations: vt = virtual triplet; $N = {}^3J(\mathrm{PH}) + {}^5J(\mathrm{PH})$ or ${}^1J(\mathrm{PC}) + {}^3J(\mathrm{PC})$). **2**: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 4.25 (br s, 1 H, IrOH), 2.80 (m, 6 H, PC*H*CH$_3$), 1.31 (dvt, N = 13.5, ${}^3J(\mathrm{HH})$ = 7.3 Hz, 36 H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$) δ 252.8 (t, ${}^3J(\mathrm{PC})$ = 3.1 Hz, Ir=C=*C*=C), 202.7 (t, ${}^2J(\mathrm{PC})$ = 12.7 Hz, Ir=*C*=C=C), 22.6 (vt, N = 24.4 Hz, P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$), resonance of Ir=C=C=*C* not observed; ^{31}P NMR (162.0 MHz, C$_6$D$_6$) δ 23.5 (s); IR (C$_6$H$_6$) ν(OH) 3643, ν(C=C=C) 1857 cm^{-1}. **3**: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 2.81 (m, 6 H, PC*H*CH$_3$), 1.33 (dvt, N = 13.5, ${}^3J(\mathrm{HH})$ = 7.0 Hz, 36 H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$) δ 273.9 (m, Ir=C=*C*=C), 205.8 (m, Ir=*C*=C=C), 127.3 (m, Ir=C=C=*C*), 23.1 (vt, N = 25.4 Hz, P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$); ^{19}F NMR (188.0 MHz, C$_6$D$_6$) δ −145.3 (t, ${}^2J(\mathrm{PF})$ = 20.0 Hz); ^{31}P NMR (162.0 MHz, C$_6$D$_6$) δ 26.2 (d, ${}^2J(\mathrm{PF})$ = 20.3 Hz); IR (CH$_2$Cl$_2$) ν(C=C=C) 1872 cm^{-1}. **4**: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 2.60 (m, 6 H, PC*H*CH$_3$), 1.25 (dvt, N = 13.2, ${}^3J(\mathrm{HH})$ = 7.0 Hz, 36 H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$) δ 255.7 (t, ${}^3J(\mathrm{PC})$ = 3.6 Hz, Ir=C=*C*=C)], 203.6 (t, ${}^2J(\mathrm{PC})$ = 13.7 Hz, Ir=*C*=C=C), 131.8 (t, ${}^4J(\mathrm{PC})$ = 3.1 Hz, Ir=C=C=*C*), 23.8 (vt, N = 25.8 Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C$_6$D$_6$) δ 23.3 Hz (s); IR (C$_6$H$_6$) ν(C=C=C) 1868 cm^{-1}. **5**: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 9.36 (s, 1 H, *H*C=C=CPh$_2$), 7.93 (br s, 1 H, IrC*H*=C), 3.27 (m, 6 H, PC*H*CH$_3$), 1.32 (dvt, N = 13.2, ${}^3J(\mathrm{HH})$ = 6.6 Hz, 18 H, PCHC*H*$_3$), 1.27 (dvt, N = 13.2, ${}^3J(\mathrm{HH})$ = 7.0 Hz, 18 H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$) δ 211.6 (s, C=*C*=C), 177.3 (t, ${}^3J(\mathrm{PC})$ = 4.0 Hz, IrCH=*C*), 119.3 (t, ${}^2J(\mathrm{PC})$ = 12.2 Hz, Ir*C*≡C), 115.3 (t, ${}^3J(\mathrm{PC})$ = 4.1 Hz, IrC≡*C*), 111.4 (s, HC=C=*C*), 104.5 (t, ${}^2J(\mathrm{PC})$ = 8.1 Hz, Ir*C*H=C), 100.9 (s, *C*H=C=C), 24.6 (vt, N = 26.4 Hz, P*C*HCH$_3$), 20.4 and 20.2 (both s, PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C$_6$D$_6$) δ 13.0 (s); IR (C$_6$H$_6$) ν(C≡C) 2076 and 2078 cm^{-1}. **6**: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 9.40 (s, 1 H, *H*C=C=CPh$_2$), 8.63 (br s, 1 H, IrC*H*=C), 3.41 (s, 6 H, CO$_2$CH$_3$), 3.33 (s, 3 H, CO$_2$CH$_3$), 3.11 (m, 6 H, PC*H*CH$_3$), 1.13 (dvt, N = 14.0, ${}^3J(\mathrm{HH})$ = 7.0 Hz, 36 H, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$) δ 211.4 (s, C=*C*=C), 162.8 and 154.5 (both s, *C*O$_2$CH$_3$), 126.4 (t, ${}^3J(\mathrm{PC})$ = 3.5 Hz, IrC≡*C*), 123.5 (t, ${}^2J(\mathrm{PC})$ = 7.1 Hz, Ir*C*H=C), 94.2 (s, *C*H=C=C), 111.4 (s, HC=C=*C*), 51.4 and 51.3 (both s, CO$_2$CH$_3$), 25.1 (vt, N = 27.3 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$), resonances of IrCH=*C* and Ir*C*≡C not observed; ^{31}P NMR (162.0 MHz, C$_6$D$_6$) δ 16.9 (s); IR (C$_6$H$_6$) ν(C≡C) 2084 cm^{-1}, ν(OCO)$_{as}$ 1686 cm^{-1}, ν(OCO)$_s$ 1431 cm^{-1}.

(7) (a) Triethylamine tris(hydrogen fluoride) is a new, versatile fluorinating agent which has recently been used for the first time in the chemistry of late transition metals.[7b,c] (b) Fraser, S. L.; Antipin, M. Y.; Khroustalyov, V. N.; Grushin, V. V. *J. Am. Chem. Soc.* **1997**, *119*, 4769−4770. (c) Pilon, M. C.; Grushin, V. V. *Organometallics* **1998**, *17*, 1774−1781.

10.1021/om990851j CCC: $18.00
Publication on Web 12/02/1999

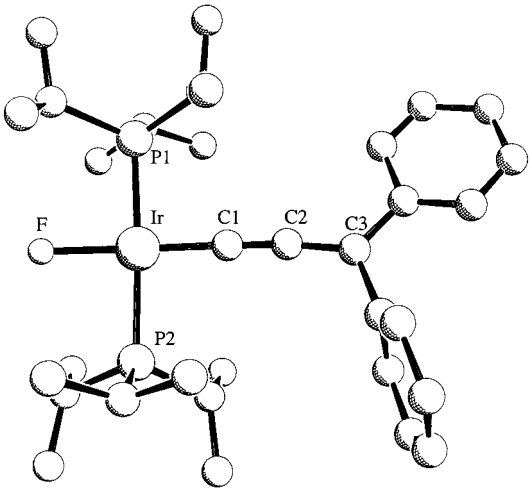
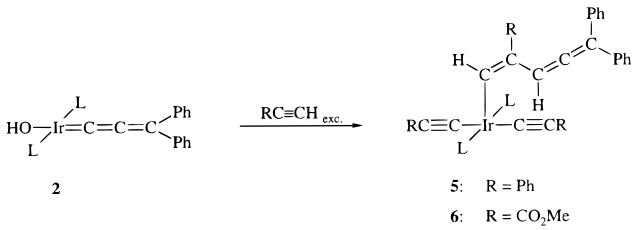


Figure 1. Molecular diagram of compound **3**. Selected bond lengths (Å) and angles (deg): Ir−F = 2.015(10), Ir−P1 = 2.317(4), Ir−P2 = 2.326(4), Ir−C1 = 1.85(2), C1−C2 = 1.22(2), C2−C3 = 1.37(2); F−Ir−P1 = 88.5(3), F−Ir−P2 = 89.0(3), F−Ir−C1 = 179.3(6), P1−Ir−P2 = 177.51(16), P1−Ir−C1 = 91.0(5), P2−Ir−C1 = 91.5(5), Ir−C1−C2 = 177.1(17), C1−C2−C3 = 173(2).

Typical spectroscopic features of **3** and **4** (both are red, only moderately air-sensitive solids) are their respective low-field signals at δ 273.9 or 255.7 (β-C) and 205.8 or 203.6 (α-C) in the ^{13}C NMR as well as the single resonance at δ 26.2 or 23.3 in the ^{31}P NMR spectra.[6] The X-ray crystal structure analysis of **3** (Figure 1) reveals an almost perfect square-planar coordination sphere around the iridium center with the two phosphines in a trans disposition.[10] The C1−C2−C3 chain is nearly linear, with the *ipso*-carbon atoms of the phenyl rings lying in the same plane as Ir, P1, P2, F, C1, C2, and C3.

Most remarkably, the hydroxo compound **2** is also highly reactive toward phenylacetylene and methyl propiolate (Scheme 2). Stirring a solution of **2** in benzene with a 10-fold excess of the alkyne for 30 min at room temperature led to a change of color from orange to violet or red and, after chromatographic workup and recrystallization from pentane, gave **5** and **6** as crystalline, slightly air-sensitive solids in 85−90% yield.[11] The elemental analyses as well as the NMR spectra of both complexes indicated that not only a substitution of the OH for the C≡CR unit but also the generation of a C_5 ligand had taken place. This proposal was confirmed by an X-ray crystal structure analysis of **5** (Figure 2).[12] The coordination sphere around the iridium center is square pyramidal, with two trans-disposed alkynyls and two trans-disposed phosphines in the basal plane and the σ-bonded CH=CPhCH=C=CPh$_2$ unit in the apical position. In contrast to the reaction of *trans*-[RhCl(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] with phenylacetylene, which affords via coupling of the allenylidene with the alkyne and one phosphine a complex containing a highly unsaturated Wittig-type ylide as a π-bonded ligand,[13] upon treatment of **2** with HC≡CPh presumably a substitution (of OH by C_2Ph), an oxidative addition (of HC≡CPh to iridium(I)), and an insertion of an alkyne molecule into an iridium−allenyl linkage occurs. The bond lengths Ir−C1, Ir−C40, and Ir−C50 differ only slightly, while the distances C3−C4 and C4−C5 are comparable to those of the substituted allenylrhodium complex *trans*-[Rh{η^1-C(CH=CH$_2$)=C=CPh$_2$}(CO)(P*i*Pr$_3$)$_2$].[13] With regard to the formation of **5** and **6**, the most noteworthy feature is that despite the strength of the Ir−C double bond in **1**[4] and the analogous compounds **2**−**4**, a coupling of the alkyne with the C_3 unit takes place under exceedingly mild conditions. It is conceivable that the insertion reaction is preceded by the generation of the iridium−hydride intermediate [IrH(C≡CR)$_2$(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$], which rearranges

Scheme 2[a]



[a] L = P*i*Pr$_3$.

(8) The preparation of **3** is as follows. A solution of **2** (69 mg, 0.10 mmol) in 10 mL of benzene was treated with NEt$_3$·3HF (5.2 μL, 0.10 mmol). An instant change of color from orange to red occurred. The solvent was removed in vacuo, the residue was extracted with 50 mL of pentane, and the extract was brought to dryness in vacuo. The oily residue was dissolved in 3 mL of acetone, and the solution was stored at −78 °C. After 24 h red crystals precipitated, which were separated from the mother liquor, washed twice with 1 mL of pentane, and dried: yield 61 mg (88%); mp 89 °C dec. Anal. Calcd for $C_{33}H_{53}FIrP_2$: C, 54.90; H, 7.26. Found: C, 55.09; H, 7.11.

(9) The preparation of **4** is as follows. A solution of **2** (57 mg, 0.08 mmol) in 10 mL of benzene was treated with phenol (7.5 mg, 0.08 mmol). An instant change of color from orange to red occurred. After the mixture was stirred at room temperature for 5 min, the solvent was removed in vacuo. The residue was extracted with 25 mL of acetone, and the extract was concentrated to 2 mL in vacuo. The solution was stored at −78 °C for 20 h, which led to the precipitation of red crystals. They were separated from the mother liquor, washed twice with small quantities of pentane (0 °C), and dried: yield 49 mg (82%); mp 86 °C dec. Anal. Calcd for $C_{39}H_{57}IrOP_2$: C, 58.84; H, 7.22. Found: C, 58.63; H, 7.45.

(10) Crystal data for **3**: crystals from acetone; crystal size 0.19 × 0.14 × 0.11 mm; monoclinic, space group $P2_1/n$ (No. 14), Z = 4; a = 8.6057(13) Å, b = 34.735 (3) Å, c = 10.8869(15) Å, β = 95.737(15)°, V = 3237.7(7) Å^3, d_{calcd} = 1.481 g cm^{-3}; 2θ(max) = 46.50° (Mo Kα, λ = 0.710 73 Å, graphite monochromator, ω/θ scan, Zr filter with factor 15.4, T = 173(2) K; 5131 reflections scanned, 4604 unique, 2743 observed ($I > 2\sigma(I)$), Lorentz−polarization and empirical absorption corrections (ψ scans, minimum transmission 90.00%); direct methods (SHELXS-97), 346 parameters, reflex/parameter ratio 13.31; R1 = 0.0661, wR2 = 0.1702; residual electron density +1.173/−1.682 e Å^{-3}.

(11) The preparation of **5** is as follows. A solution of **2** (55 mg, 0.08 mmol) in 10 mL of benzene was treated with phenylacetylene (81 μL, 0.80 mmol), and the mixture was stirred at room temperature for 30 min. A change of color from orange to violet occurred. After concentration to 1 mL in vacuo, the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With pentane a violet phase was eluted and brought to dryness in vacuo. The oily residue was recrystallized from pentane at −78 °C: yield 70 mg (87%); mp 53 °C dec. Anal. Calcd for $C_{57}H_{63}IrP_2$: C, 67.90; H, 6.90. Found: C, 68.01; H, 7.04. Compound **6** was prepared analogously, using **2** (57 mg, 0.08 mmol) and methyl propiolate (50 μL, 0.80 mmol) as starting materials: red microcrystalline solid; yield 71 mg (89%); mp 62 °C dec. Anal. Calcd for $C_{45}H_{63}IrO_6P_2$: C, 56.65; H, 6.66. Found: C, 56.95; H, 6.51.

(12) Crystal data for **5**: crystals from diethyl ether; crystal size 0.21 × 0.18 × 0.16 mm; triclinic, space group $P\bar{1}$ (No. 2), Z = 2; a = 13.600(4) Å, b = 13.634(4) Å, c = 14.994(4) Å, α = 83.29(2)°, β = 66.63-(3)°, γ = 87.23(2)°, V = 2537.8(13) Å^3, d_{calcd} = 1.319 g cm^{-3}; 2θ(max) = 44.92° (Mo Kα, λ = 0.710 73 Å, graphite monochromator, ω/θ scan, Zr filter with factor 15.4, T = 193(2) K; 6946 reflections scanned, 6598 unique, 5794 observed ($I > 2\sigma(I)$), Lorentz−polarization and empirical absorption corrections (ψ scans, minimum transmission 84.03%); direct methods (SHELXS-97), 598 parameters, reflex/parameter ratio 11.03; R1 = 0.0370, wR2 = 0.0718; residual electron density +0.620/−1.097 e Å^{-3}.

(13) Wiedemann, R.; Steinert, P.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1996**, *118*, 2495−2496.

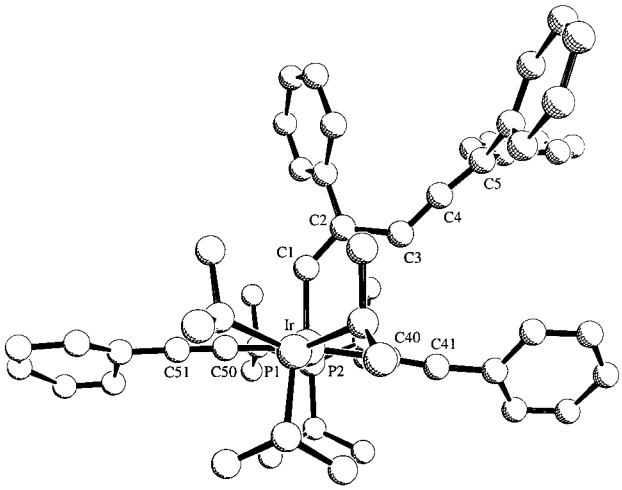


Figure 2. Molecular diagram of complex **5**. Selected bond lengths (Å) and angles (deg): Ir−C1 = 1.998(6), Ir−C40 = 2.020(6), Ir−C50 = 2.018(6), Ir−P1 = 2.359(2), Ir−P2 = 2.371(2), C1−C2 = 1.35(1), C2−C3 = 1.46(1), C3−C4 = 1.32(1), C4−C5 = 1.31(1); C1−Ir−C40 = 98.0(2), C1−Ir−C50 = 89.5(2), C1−Ir−P1 = 95.1(2), C1−Ir−P2 = 96.7(2), C40−Ir−C50 = 172.4(3), C40−Ir−P1 = 92.2(2), C40−Ir−P2 = 89.3(2), C50−Ir−P1 = 87.7(2), C50−Ir−P2 = 89.3-(2), P1−Ir−P2 = 167.77(6), Ir−C1−C2 = 135.8(5), C1−C2−C3 = 125.0(6), C2−C3−C4 = 127.9(6), C3−C4−C5 = 175.1(6), Ir−C40−C41 = 176.9(5), Ir−C50−C51 = 177.9-(6).

to a metal−allenyl species that undergoes the C−C coupling process.

In summary, the results reported in this paper illustrate that although complexes of the late transition metals with a hydroxo ligand are thermodynamically stable,[14] the M−OH bond is nevertheless rather labile and can be cleaved even by weak proton sources. In this respect, our work complements recent studies by Milstein[15] and Bergman,[16] which showed that both hydroxo− and alkoxo−iridium(III)—not iridium(I)—compounds are useful starting materials for carrying out substitution, elimination, and insertion reactions. We are currently attempting to elucidate the exact mechanism of the formation of the novel Ir−C_5 moiety and to find a route to couple the C_5 unit with one of the alkynyl ligands.

Acknowledgment. We are grateful for financial support of this work from the Deutsche Forschungsgemeinschaft (SFB 347) and the Fonds der Chemischen Industrie. We also thank Dr. Justin Wolf for helpful advice.

Supporting Information Available: Tables of crystallographic data, data collection, solution and refinement details, positional and thermal parameters, and both distances and angles for **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990851J

(14) (a) Bryndza, H. E.; Fong, K. L.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444−1456. (b) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163−1188.

(15) (a) Blum, O.; Milstein, D. *Angew. Chem.* **1995**, *107*, 210−212; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 229−231. (b) Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 4582−4594.

(16) (a) Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7888−7889. (b) Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 2580−2581. (c) Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6826−6827.