Orthometalation of Tp*Rh(PPh$_3$)$_2$: Implications for Catalytic Reactivity

Changsheng Cao, Tongen Wang, Brian O. Patrick, and Jennifer A. Love*

Department of Chemistry, 2036 Main Mall, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada

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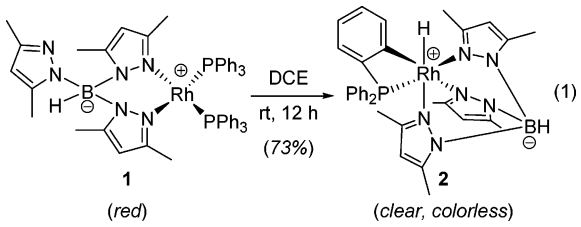
*Summary: In the course of our studies of the catalytic reactivity of Tp*Rh(PPh$_3$)$_2$ (**1**), we noted considerable decomposition of **1** in reactions conducted in 1,2-dicholoroethane (DCE) requiring extended reaction times (>12 h). Because this decomposition could have significant implications for the catalytic utility of **1**, we have undertaken a study of the decomposition process. We herein report that **1** undergoes facile, irreversible orthometalation of a PPh$_3$ ligand at room temperature in slightly polar solvents, such as THF and 1,2-dichloroethane. In comparison, orthometalation is virtually undetectable in PhCH$_3$ at room temperature. Fortunately, **1** shows catalytic activity for hydrothiolation and hydrophosphinylation in low-polarity solvents. Accordingly, reactions using **1** (and potentially related complexes) should be conducted in nonpolar solvents or solvent mixtures whenever possible.*

Introduction

Hydrotris(pyrazolyl)borates (Tp^R, R = H, alkyl, aryl, or halide) are widely used as ligands for transition metals.[1] Although rhodium pyrazolylborates have been extensively studied for stoichiometric C−H activation reactions,[2,3] the catalytic reactivity of these complexes has received considerably less attention.[2,4] We have recently disclosed that Tp*Rh(PPh$_3$)$_2$ (**1**, Tp* = hydrotris(3,5-dimethylpyrazolyl)borate)[5] catalyzes the hydrothiolation of aryl alkynes with both aryl and alkyl thiols,[6] as well as the hydrophosphinylation of alkynes.[7] In the course of our studies, we noticed that **1** decomposed over a period of several hours at room temperature in both THF and 1,2-dichloroethane (DCE). Decomposition was accompanied by a decrease in reaction rate, suggesting that sluggish reactions (i.e., those requiring >12 h) would be further impeded by depletion of the catalyst. Consequently, suppressing this decomposition was deemed crucial to the catalytic utility of **1**. Given the recent interest in Tp^{R}Rh(PR$_3$)$_2$ complexes,[4−8] preventing the decomposition of **1** could impact a variety of catalytic and stoichiometric transformations. For these reasons, we decided to investigate the decomposition and to elucidate the structure of the decomposition product.

Results and Discussion

When a solution of **1** in DCE is maintained at room temperature for 12 h, a dramatic color change from red to pale yellow is observed. The ^{1}H NMR spectrum of a reaction aliquot exhibited a characteristic Rh−H resonance at −14.21 ppm, with coupling to both phosphorus and rhodium. The ^{31}P NMR spectrum revealed free PPh$_3$ and a new doublet at −32.65 ppm, which is significantly shifted upfield relative to **1** (43.63 ppm); such a shift is diagnostic for orthometalation of a phosphine ligand.[9] The ^{103}Rh−^{31}P coupling constant of 110 Hz is within the normal range.[10] These data are consistent with loss of 1 equiv of PPh$_3$ followed by orthometalation of the remaining PPh$_3$ ligand (eq 1). The product (**2**) was isolated in 73% yield.



Orthometalation of a triphenylphosphine ligand is well-precedented for rhodium,[11] as well as other late transition metals.[8,12] Although both Tp*Rh(PPh$_3$)$_2$ and TpRh(PPh$_3$)$_2$ (Tp = hydrotris(pyrazolyl)borate) undergo a variety of stoichiometric reactions, including C−H activation, cyclometalation reactions

* To whom correspondence should be addressed. E-mail: jenlove@chem.ubc.ca.

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have not been reported.[13,14] In comparison, a closely related complex, $TpIr(PPh_3)_2$, undergoes reversible cyclometalation of one of the pyrazole rings.[15]

The structure of **2** was confirmed by X-ray crystallographic analysis and is similar to other crystallographically characterized four-membered metallacycles.[9a,11] For example, the Rh−P and Rh−C bond lengths of **2** fall within the range reported for related complexes by Bennett and Bianchini.

Complex **2** is formed under a variety of reaction conditions. When **1** is left in DCE or THF solution, orthometalation occurs within a few hours at room temperature. In comparison, orthometalation does not occur even after prolonged time (2 months) in $PhCH_3$ at room temperature. Not surprisingly, the formation of **2** occurs rapidly even in $PhCH_3$ at elevated temperatures (within hours at 80 °C and within minutes at 130 °C).

Complex **2** also forms during the preparation of **1** from Wilkinson's catalyst $[RhCl(PPh_3)_3]$ and KTp* in THF if the reaction is allowed to proceed for longer than 2 h. This reaction presumably occurs through initial substitution of Tp* for Cl to form **1**, followed by orthometalation. As reactions to prepare $Tp^RRh(PPh_3)_2$ complexes are best run in THF to ensure reasonable reaction rates (presumably due to the insolubility of KTp^R in less polar solvents), these reactions should be carefully monitored to prevent orthometalation. Indeed, we obtained a notably higher yield for the synthesis of **1** than had been previously reported, which we attribute to the shorter reaction time in our synthetic protocol.[6]

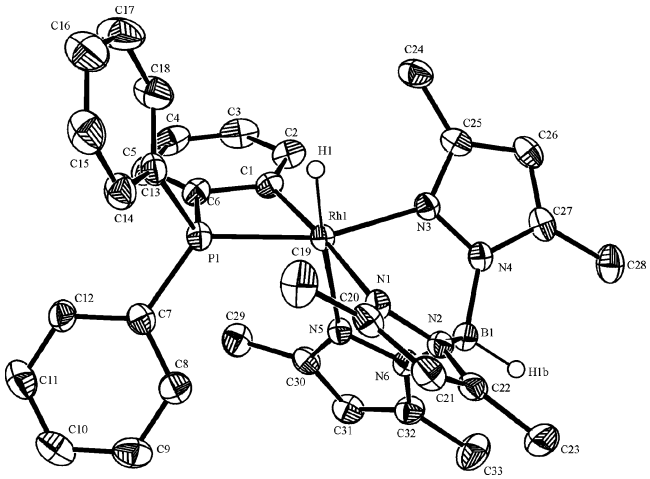

Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Most hydrogen atoms are excluded for clarity. Selected bond lengths (Å) and angles (deg): Rh−P = 2.2694(6), Rh−C(1) = 2.025(2), C(1)−C(6) = 1.411(3), C(6)−P = 1.806(2), Rh−H = 1.48(3), C(6)−C(1)−Rh = 107.05(1), C(1)−C(6)−P = 97.97(1), C(1)−Rh−P = 69.02(6), C(1)−Rh−H = 87.6(9), P−Rh−H = 78.7(9).

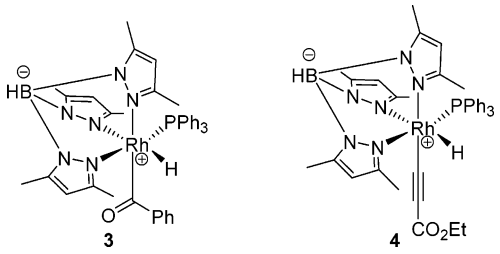

Figure 2. Complexes **3** and **4**.

We have also observed the formation of **2** from related rhodium complexes **3** and **4** (Figure 2) that bear both a Tp* and PPh_3 ligand.[16] Spectroscopic and elemental analyses of solid-state samples of **3** and **4** that had been kept at 0 °C for several months revealed that both samples had quantitatively converted to **2**. These observations suggest that formation of **2** is highly favorable.

Given the ease of formation of **2** in moderately polar solvents, this type of decomposition pathway could potentially complicate the use of **1** in catalysis unless **2** is formed irreversibly or formation of **2** can be suppressed. Complex **2** exhibited no reactivity under typical conditions for either alkyne hydrothiolation[6] or hydrophosphinylation;[7] the observation that **2** cannot generate an active catalyst is consistent with irreversible orthometalation.[17,18]

These results indicate that suppression of orthometalation is crucial for efficient catalysis, particularly considering that some hydrothiolation reactions require several hours to reach comple-

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(13) A related complex, $Tp^{i-Pr2}Rh(dppe)$ [dppe = 1,2-bis(diphenylphosphino)ethane], undergoes phosphine oxidation with O_2, followed by orthometalation to the corresponding five-membered ring complex. Takahashi, Y.; Hashimoto, M.; Hikichi, S.; Moro-oka, Y.; Akita, M. *Inorg. Chim. Acta* **2004**, *357*, 1711−1724.

(14) Upon irradiation, $Tp^{Me2,Cl}Rh(CO)_2$ reacts with diisopropylamine to generate a four-membered cyclometalated complex. Teuma, E.; Malbosc, F.; Pons, V.; Serra-Le Berre, C.; Jaud, J.; Etienne, M.; Kalck, P. *J. Chem. Soc., Dalton Trans.* **2001**, *15*, 2225−2227.

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(16) Using a procedure similar to that used by Carlton (see ref 5b) for the formation of $Tp*Rh(H)(COPh)(PPh_3)$ and $Tp*Rh(H)(CCPh)(PPh_3)$ from **1**, complexes **3** and **4** were formed by oxidative addition of the benzaldehyde and ethylpropiolate, respectively, and loss of 1 equiv of PPh_3. Formation of both **3** and **4** were accompanied by orthometalation. The X-ray structures of **3** and **4** bear a close resemblance to structures of the related complexes reported by Carlton and are presented in the Supporting Information.

(17) Of the known late transition metal complexes containing an orthometalated PPh_3 ligand, a few were found to have been formed irreversibly. For examples, see: (a) Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, *21*, 4050−4064. (b) Ref 14.

(18) For an example of reversible orthometalation, see ref 11f.

tion.[6] Fortunately, simply using a slightly less polar solvent combination (1:1 DCE/$PhCH_3$) precludes decomposition without compromising rate, yield, or regioselectivity, even for prolonged reaction times (>20 h).[6] Importantly, orthometalation is not observed at room temperature in a 1:1 mixture of DCE/$PhCH_3$, consistent with the stability of **1** in pure $PhCH_3$. Evidently, even subtle changes in solvent polarity can significantly impact the rate of orthometalation, suggesting that reactions using **1** are best conducted in low-polarity solvents whenever possible.

Conclusion

Tp*Rh(PPh_3)$_2$ (**1**) and related complexes decompose by orthometalation of a PPh_3 ligand to form **2** when kept in moderately polar solution over a period of several hours. This process is essentially irreversible, despite the strain inherent in the four-membered ring. Nevertheless, orthometalation can be suppressed with judicious selection of solvent. As such, nonpolar solvents are preferable for reactions using **1**.

Experimental Section

General Procedures. Manipulation of organometallic compounds was performed using standard Schlenk techniques under an atmosphere of dry nitrogen or in a nitrogen-filled Vacuum Atmospheres or MBraun drybox (O_2 < 2 ppm). NMR spectra were recorded on Bruker Avance 300 or Bruker Avance 400 spectrometers. ^{1}H and ^{13}C NMR spectra are reported in parts per million and were referenced to residual solvent. ^{31}P NMR spectra were referenced to an external 85% H_3PO_4 standard. All spectra were obtained at 25 °C. Coupling constant values were extracted assuming first-order coupling. The multiplicities are abbreviated as follows: s = singlet, d = doublet, m = multiplet, br = broad signal, dd = doublet of doublets. Elemental analyses were performed using a Carlo Erba EA 1108 elemental analyzer. GC spectra were recorded on a Varian CP-3800 or an HP 5890 Series II gas chromatograph. Mass spectra were recorded on a Varian 1200L GC-MS or a Kratos MS-50 mass spectrometer.

Materials and Methods. Hexane, 1,2-dichloroethane, THF, and toluene were dried by passage through solvent purification columns.[19] $CDCl_3$ was dried by vacuum transfer from P_2O_5 and was degassed prior to use. All organic reagents were obtained from commercial sources and used as received. Wilkinson's catalyst, ClRh(PPh_3)$_3$, was purchased from Strem Chemicals and was used without further purification. Rhodium complex **1** was prepared by a modification[6] of the published procedures.[5]

Preparation of 2 from Tp*Rh(PPh_3)$_2$. Rh(Tp*)(PPh_3)$_2$ (100 mg, 0.108 mmol) was dissolved in DCE (3 mL) in a 20 mL vial equipped with a screw cap and a magnetic stir bar. The solution was stirred for 12 h at room temperature. During this time, the solution changed from red to pale yellow. The volatiles were removed under reduced pressure at room temperature. The residue was dissolved in toluene (10 mL), filtered through Celite, and condensed to ~2 mL. The product was crystallized by layering hexane onto the toluene solution. The resulting clear, colorless crystals were collected by filtration. The remaining solvent was evaporated to yield 52 mg (73% yield) of Tp*Rh(H)(*o*-$C_6H_4PPh_2$) (**2**). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.80−7.60 (m, 4H), 7.384 (m, 1H), 7.07−6.70 (m, 9H), 5.774 (s, 1H), 5.644 (s, 1H), 5.534 (s, 1H), 5.40−4.50 (br, 1H), 2.61 (s, 3H), 2.27 (d, J = 3.244 Hz, 6H), 2.24 (s, 3H), 1.87 (s, 3H), 0.95 (s, 3H), −14.21 (dd, J_1 = 32 Hz, J_2 = 19.6 Hz, 1H). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 152.2, 151.7, 150.5, 143.6, 143.2, 138.6, 138.1, 135.4, 134.7, 132.8, 131.5, 131.2, 130.7, 130.2, 129.5, 128.6, 128.2, 127.9, 125.3, 123.1, 107.2, 106.1, 105.6, 16.3, 16.0, 13.0, 12.84, 12.81, 12.3. ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ −32.65 (d, J_{Rh-P} = 110 Hz). HRMS (EI): *m*/*z* calcd for $C_{33}H_{37}BN_6PRh$ 662.1965; found 662.1962. Anal. Calcd for $C_{33}H_{37}BN_6PRh$: C, 59.84; H, 5.63; B, 1.63; N, 12.69; P, 4.68; Rh, 15.54. Found: C, 60.24; H, 5.82; N, 12.69.

Preparation of 2 from ClRh(PPh_3)$_3$. ClRh(PPh_3)$_3$ (100 mg, 0.108 mmol) and hydrotris(3,5-dimethylpyrazol-1-yl)borate (0.0375 mg, 0.112 mmol) were combined in a 20 mL vial equipped with a screw cap and a magnetic stir bar and were dissolved in THF (3 mL). The solution was stirred for 12 h at room temperature. During this time, the solution changed from red to pale yellow and a pale yellow precipitate appeared. The volatiles were removed under reduced pressure at room temperature. The residue was dissolved in toluene (10 mL), filtered through Celite, and condensed to ~2 mL. The product was crystallized by layering hexane onto the toluene solution. The resulting clear, colorless crystals were collected by filtration. The remaining solvent was evaporated to yield 54 mg (76% yield) of Tp*Rh(H)(*o*-$C_6H_4PPh_2$) (**2**).

Preparation of 3 from Tp*Rh(PPh_3)$_2$. Rh(Tp*)(PPh_3)$_2$ (100 mg, 0.108 mmol) was dissolved in DCE (2 mL) in a 20 mL Schlenk tube equipped with a glass stopper and a magnetic stir bar, and benzaldehyde (13.8 mg, 0.130 mmol) was added. The solution was stirred for 1 h at 130 °C. The volatiles were removed under reduced pressure at room temperature. The residue was dissolved in toluene (10 mL), filtered through Celite, and condensed to ~2 mL. The product was crystallized by layering hexane onto the toluene solution. The resulting clear, colorless crystals were collected by filtration. The remaining solvent was evaporated to yield 53 mg (64% yield) of Tp*Rh(H)(COPh)(PPh_3) (**3**). A significant amount of **2** (not isolated) was also formed. This procedure is variable and gives mixtures of **2** and **3**. Complex **3** was isolated by selective crystallization on one occasion. Selected analytical data, determined by measuring NMR spectra of a mixture of **2** and **3**, are reported as follows. ^{1}H NMR (d_8-toluene, 300 MHz): δ −13.41 (dd, 1H, J = 19 Hz, J = 12 Hz, Rh-*H*). ^{31}P{^{1}H} NMR (d_8-toluene, 121 MHz): δ 49.54 (d, J = 165 Hz).

Preparation of 4 from Tp*Rh(PPh_3)$_2$. Rh(Tp*)(PPh_3)$_2$ (100 mg, 0.108 mmol) was dissolved in DCE (2 mL) in a 20 mL Schlenk tube equipped with a glass stopper and a magnetic stir bar, and ethyl propiolate (10.6 mg, 0.108 mmol) was added. The solution was stirred for 2 h at 100 °C. The volatiles were removed under reduced pressure at room temperature. The residue was dissolved in toluene (10 mL), filtered through Celite, and condensed to ~2 mL. The product was crystallized by layering hexane onto the toluene solution. The resulting clear, colorless crystals were collected by filtration. The remaining solvent was evaporated to yield 58.3 mg (71% yield) of Tp*Rh(H)(CCCO$_2$Et)(PPh_3) (**4**). A significant amount of **2** (not isolated) was also formed. This procedure is variable and gives mixtures of **2** and **4**. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.87 (m, 6H), 7.00 (m, 9H), 5.60 (s, 1H), 5.42 (s, 1H), 5.06 (s, 1H), 3.99 (q, 2H, J = 7.1 Hz), 3.07 (s, 3H), 2.42 (s, 3H), 2.22 (s, 3H), 2.08 (s, 3H), 1.66 (s, 3H), 1.53 (s, 3H), 0.95 (t, 3H, J = 7.2 Hz), −13.98 (dd, 1H, J = 21.6 Hz, J = 16.8 Hz), B−H not observed. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 155.45, 154.05, 151.90, 150.86, 145.03, 144.43, 143.52, 136.81, 136.11, 136.01, 133.80, 133.31, 130.59, 108.20, 106.66, 102.45, 60.08, 17.20, 16.74, 14.83, 13.32, 13.14, 13.07, 12.78. ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 46.04 (J = 129 Hz). HRMS (EI): *m*/*z* calcd for $C_{38}H_{43}BN_6O_2PRh$ 760.2333; found 760.2339. Anal. Calcd for $C_{38}H_{43}BN_6O_2PRh$: C, 60.02; H, 5.70; B, 1.42; N, 11.05; O, 4.21; P, 4.07; Rh, 13.53. Found: C, 60.30; H, 5.94; N, 11.38.

X-ray Crystal Structures of 2, 3, and 4. Crystal, intensity collection, and refinement details are summarized in the Supporting Information as Tables S1, S7, and S13. All measurements were made on a Bruker X8 APEX diffractometer with graphite-monochromated Mo Kα radiation. Data were collected in a series of ϕ and ω scans and subsequently processed with the Bruker

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SAINT[20] software package. Data were corrected for absorption effects using the multiscan technique (SADABS).[20] The data were corrected for Lorentz and polarization effects. The structures were solved using direct methods[21] and refined using SHELXTL.[20] For complexes **2** and **4**, all B-H and Rh-H hydrogen atoms were located in difference maps, while all other hydrogen atoms were included in calculated positions but not refined. For complex **3**, all non-hydrogen atoms except the benzene atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined, except for the B- and Rh-hydrides, which were located in difference maps and refined isotropically. Pertinent bond lengths and angles are presented in the caption of Figure 1 for **2**. Full details for **2**, **3**, and **4** are presented in the Supporting Information.

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Supporting Information Available: Crystallographic data (labeled drawings, table of atomic coordinates, complete bond distances and angles, and anisotropic displacement parameters) for complexes **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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