Cyclometalation of a Pyrazolyl Arm in Hydridotris(1-pyrazolyl)borate and Tris(1-pyrazolyl)methane Complexes of Iridium

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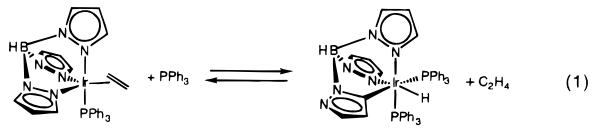
Received July 8, 1996

The synthesis and reactions of hydridotris(1-pyrazolyl)borate (Tp^{R2}, R = H or Me) complexes[1] of rhodium and iridium have recently been the focus of much interest due to their role in C−H bond activation reactions.[2−8] Specifically, the Tp^{Me2} complexes have received the most attention, due in part to the observation that methyl substituents in the 3- and 5-positions stabilize against thermal decomposition. For example, $TpIr(C_2H_4)_2$ is reported to decompose at 70 °C to a complex mixture of products,[9] whereas $Tp^{Me2}Ir(C_2H_4)_2$ cleanly isomerizes at 60 °C, first to the vinyl hydride complex $Tp^{Me2}Ir(C_2H_4)(CH{=}CH_2)$-H[10] and then to other products,[11,12] depending on experimental conditions. The $TpIr(C_2H_4)(CH{=}CH_2)H$ complex is not intrinsically unstable, evidenced by the fact that it can be formed in high yield under photochemical conditions. The difference in thermal reactivity is curious if one considers that the unsubstituted Tp ligand may actually afford greater steric protection of the metal center because it is more likely to adopt a tridentate structure (e.g., η^3-$TpIr(CO)(C_2H_4)$[13] vs η^2-$Tp^{Me2}Ir(CO)(C_2H_4)$[3,5]). However, even when the ground state structure is trigonal bipyramidal (tbp), four-coordinate square planar (sp) species are thermally accessible.[14−17]

In this paper, we report observations of a previously unknown cyclometalation reaction of the Tp ligand. This reaction leads to formal oxidation of the iridium center by formation of an iridium(III) alkyl hydride complex *via* activation of a C−H bond of a pyrazolyl ring. We have also observed similar chemistry in a related cationic iridium complex of tris(1-pyrazolyl)methane (Tpm).

Methylene chloride solutions of $TpIr(PPh_3)(C_2H_4)$ (**1**)[18] and a 6-fold excess of PPh_3 react to form equilibrium mixtures of **1** and the cyclometalated complex (N,C^5,N-Tp)$Ir(PPh_3)_2H$ (**2**) and free ethylene upon standing for 20 h (eq 1). These reactions



1 2 (1)

were conducted under vacuum in sealed NMR tubes. The relative concentration of each species was determined at equilibrium by integration of the appropriate resonances in the ^1H NMR spectra. No intermediates were detected. The equilibrium constant for eq 1 was calculated as $[\mathbf{2}][C_2H_4]/[\mathbf{1}][PPh_3]$ and equals 0.1 at room temperature ($\Delta G° = 1.4$ kcal/mol). Because a significant fraction of the displaced ethylene dissociates into the headspace, the observed ratio of **2**:**1** is *ca*. 10:1. Addition of ethylene (1 atm) results in the regeneration of **1** at the expense of **2** over several hours. In a separate experiment, addition of H_2 to a similar equilibrium mixture gives $TpIr(PPh_3)H_2$,[18] free PPh_3, and free ethylene upon standing overnight. Complete conversion to **2** was accomplished on a preparative scale by reaction of **1** with a 6-fold excess of PPh_3 in CH_2Cl_2 solutions while periodically purging the system with argon.[19]

Characterization of **2** was accomplished by ^1H, ^{31}P, and ^{13}C NMR, IR, and FABMS analyses.[20] In the ^1H NMR spectrum, the 4-pz (pz = pyrazolyl) resonance of the cyclometalated pyrazolyl arm shifts significantly upfield from 5.93 ppm in **1** to 4.76 ppm in **2**. The new resonance at 4.76 ppm appears as an apparent triplet ($J = 1.4$ Hz) due to overlap of an H−H coupling and a *trans*-P−H coupling[21] of the same magnitude. This assignment and those of the remaining pyrazolyl protons were established through a series of ^1H NMR NOE experiments. Irradiation of the hydride resonance at −18.95 ppm gives enhancement of b (4.76 ppm) and f (6.81 ppm) and of the *ortho*-phenyl protons (6.92 and 7.25 ppm). Irradiation of each pyrazolyl resonance in turn confirms the assignments shown in Figure 1. The assignments of the pyrazolyl proton resonances were used in a $^1H/^{13}C$ HETCOR experiment to assign the ^{13}C resonances of the proton-bearing carbon atoms of the pyrazolyl rings.

The complex contains two PPh_3 ligands, one of which is trans to the C^5-pyrazolyl donor. The sixth site of the octahedron is occupied by a hydride ligand, which was identified in solution by a characteristic resonance at −18.95 ppm (dd, $J_{PH} = 21.1$ and 11.7 Hz) in the ^1H NMR spectrum. When the preparation of **2** is carried out with PPh_3-d_{15}, the ^1H NMR spectrum lacks phenyl resonances but is otherwise unchanged, confirming that the hydride does not arise from phosphine cyclometalation. In the solid state, a weak IR absorption at 2179 cm^{-1} is attributed to ν_{Ir-H} while a band at 2473 cm^{-1} was assigned to ν_{B-H} of the N,C^5,N-Tp ligand. This value is unremarkable and implies that cyclometalation has little effect on the B-H vibrational mode. The doublet of doublets pattern of the hydride resonance is consistent with *cis*-P−H coupling to two inequivalent phosphine ligands. This was confirmed by $^{31}P\{$aromatic $^1H\}$ NMR experiments, which reveal resonances at 3.80 and 1.02 ppm due to an AMX spin system ($J_{PP} = 10$ Hz). These observations

(1) Substitution of the Tp ligand is represented by superscripts as suggested by Trofimenko. For example, methyl substituents in the 3,5-positions are indicated as Tp^{Me2}. For a comprehensive review of this class of complexes, see: Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980.

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(19) Clean formation of **2** requires excess PPh_3, providing isolated samples of **2** unfortunately contaminated with residual PPh_3.

(20) Selected data for **2**: ^1H NMR (CD_2Cl_2, 500 MHz) 7.86 (d, 1 H, H_e), 7.47 (m, 1 H, H_h), 6.80 (m, 1 H, H_f), 6.78 (m, 1 H, H_a), 6.54 (d, 1 H, H_c), 5.83 (t, 1 H, H_d), 5.43 (m, 1 H, H_g), 4.76 (t, 1 H, H_b), 7.37 (excess PPh_3), 7.25, 7.16, 7.08, 7.02, 6.92 (phenyl resonances of bound phosphine), −18.95 (dd, $J_{PH} = 11.7$ and 21.1 Hz, 1 H, Ir-H); ^{13}C NMR (CD_2Cl_2, 125 MHz) 144.9 (C_a), 143.6, (C_c), 138.6 (d, $J_{PC} = 8.5$ Hz, C_f), 135.3 (C_e), 134.6 (C_h), 114.4 (d, $J_{PH} = 8$ Hz, C_b), 105.5 (C_g), 105.4, (C_d); $^{31}P\{$aromatic $^1H\}$ NMR 3.80 (t, $J_{PP} = 10$ Hz, $J_{HP} = 10$ Hz), 1.02 (dd, $J_{PP} = 10$ Hz, $J_{HP} = 20$ Hz); IR 2473 (ν_{BH}), 2179 (ν_{IrH}); FABMS *m/z* 930 (M^+).

(21) All complexes of the [TpM(PR_3)] (M = Rh or Ir) fragment reveal a 1−2 Hz PH coupling in the proton resonances of the pyrazolyl arm positioned trans to the PR_3 ligand. See ref 18.

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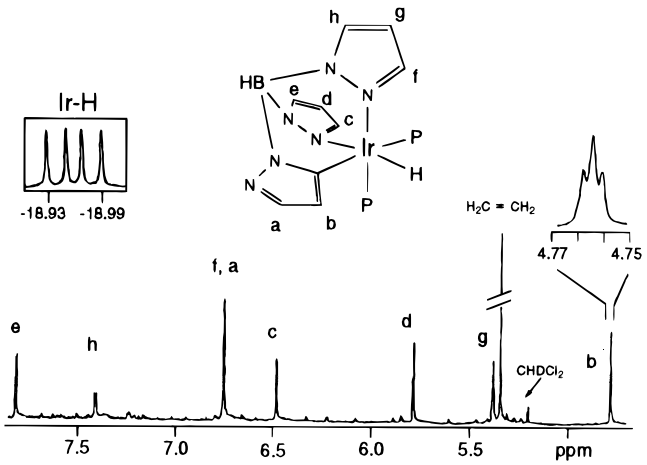
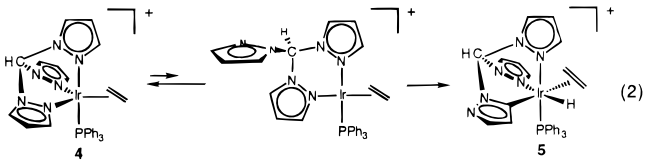


Figure 1. Partial ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of (N,C^5,N-Tp)Ir(PPh_3-d_{15})$_2$H (**2**) in CD_2Cl_2. Assignments of resonances a−h are based on NOE experiments (see text).

indicate that a cyclometalated N,C^5,N-Tp ligand is coordinated to the iridium center of **2** by way of nitrogen donors for two of the pyrazolyl arms and through the C^5-carbon atom of the activated pyrazolyl arm (see Figure 1).

We have undertaken a study of closely related Tpm complexes[22] in order to gain an understanding of the mechanism of pyrazolyl cyclometalation. Thus, [(Tpm)Ir(C_2H_4)$_2$]BF_4 (**3**)[23] reacts at −78 °C with 1 equiv of PPh_3 to form [(Tpm)Ir(PPh_3)(C_2H_4)]BF_4 (**4**)[24] and free ethylene. Upon warming to −10 °C, **4** is observed by ^{1}H NMR spectroscopy to isomerize ($t_{1/2}$ = 5.5 h) to the cyclometalated complex [(N,C^5,N-Tpm)Ir(PPh_3)(C_2H_4)H]BF_4 (**5**) (eq 2).[25] Complex **5** is thermally unstable and



(2)

slowly decomposes to a complex mixture of products. It was possible to collect spectroscopic data to support the N,C^5,N-Tpm formulation since decomposition proceeds more slowly than cyclometalation.[26] As found for **2**, cyclometalation causes a marked upfield shift of the 4-pz proton from 6.21 ppm in **4** to 4.94 ppm in **5**. The coupling pattern of the cyclometalated 4-pz resonance is now a simple doublet (J = 1.6 Hz), coupling to only one neighboring hydrogen. The hydride ligand is identified at −17.14 ppm (d, J_{PH} = 18.8 Hz). No change in the course of this reaction is observed if the reaction is carried out with an excess of PPh_3. Complex **4** can be trapped by H_2 (6 atm) at −20 °C to obtain [(Tpm)Ir(PPh_3)$_2$H$_2$]BF_4 (**6**) and free ethylene.

We have previously shown that **1** adopts a tbp structure in solution with PPh_3 coordinated in the axial site and ethylene positioned in the equatorial plane. A facile equilibrium with an unobserved sp intermediate was proposed on the basis of kinetic data for the reaction of **1** with H_2.[18] The spectroscopic data for **4** also supports a tbp structure. The isomerization of **4** to the cyclometalated complex **5** is convincing evidence that an equilibrium with a sp intermediate occurs. We have found that **5** fails to react with excess PPh_3. In fact, a number of reports in the literature have commented that iridium(III) alkene complexes stabilized by Tp^{R2} ligands are inert to substitution of the ethylene ligand under thermal conditions.[9,27,28] Similarly we have found that the ethylene ligand is not displaced from [TpIr(PPh_3)(C_2H_4)H]BF_4 (**7**)[29] or TpIr(C_2H_4)(C_2H_5)Cl (**8**) upon addition of excess PPh_3. With this in mind we rule out (N,C^5,N-Tp)Ir(PPh_3)(C_2H_4)H as a possible intermediate in the formation of **2**. Instead, we propose that **1** reacts with PPh_3 to form TpIr(PPh_3)$_2$ (**9**) which then rapidly cyclometalates (eqs 3 and 4).

$$\underset{\mathbf{1}}{\mathrm{TpIr(PPh_3)(C_2H_4)}} + \mathrm{PPh_3} \rightleftarrows \underset{\mathbf{9}}{\mathrm{TpIr(PPh_3)_2}} + \mathrm{C_2H_4} \quad (3)$$

$$\underset{\mathbf{9}}{\mathrm{TpIr(PPh_3)_2}} \rightleftarrows \underset{\mathbf{2}}{(N,C^5,N\text{-Tp})\mathrm{Ir(PPh_3)_2H}} \quad (4)$$

The structure of **9** is unknown, but this complex probably exists as a mixture of tbp and sp forms in solution.

Cyclometalation represents an unprecedented mode of reactivity for the ubiquitous Tp ligand. For low-valent iridium complexes, this reaction is feasible due to the strong Ir−C and Ir−H bonds formed by oxidative addition of the pyrazolyl C−H bond. These are the same attributes which make complexes of this type useful in alkane activation reactions, and we suggest that cyclometalation may be a common reaction for Tp complexes of transition metals in the d^8 configuration.

We have also shown that cyclometalation of the Tpm ligand occurs readily. There is precedent for this reaction in platinum(II) complexes, but the driving force of methane elimination was apparently required.[30] For example, (Tpm)Pt(CH_3)$_2$ is reported to isomerize to (η^2-N,C^5-Tpm)Pt(CH_3)(py) in hot pyridine.[31] The resulting Pt alkyls are thermally robust. In contrast, **2** and **5** retain both the alkyl and hydride ligands resulting from pyrazolyl cyclometalation and are thermally quite unstable. In solution at room temperature, complexes **2** and **5** decompose within 4−5 days or within 5 min, respectively. We suggest that the thermal stability of low-valent Tp^{Me2} complexes may be due to protection from pyrazolyl cyclometalation reactions provided by the methyl substituents. Efforts are currently underway to determine the range of coligands which promote cyclometalation of the Tp ligand in low-valent iridium complexes. We are also investigating the subsequent decomposition pathways of these cyclometalated complexes.

Acknowledgment. This work was supported by the National Science Foundation. We are grateful for fellowship support (W.J.O.) from the Chevron Research and Technology Company. We thank Miss Susan P. Millar and Dr. Ross Lawrence for obtaining the FABMS analysis of **2**.

Supporting Information Available: Experimental details and characterization data for compounds **2**−**8** (6 pages). See any current masthead page for ordering and Internet access instructions.

JA962320H

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(24) Selected data for **4**: ^{1}H NMR (CD_2Cl_2, 220 K) 9.24 (s, 1 H, *H*Cpz$_3$), 8.39, 7.26 (d, 2 H each, 3,5-pz$_{eq}$), 8.34, 7.39 (d, 1 H each, 3,5-pz$_{ax}$), 7.52−7.43, 7.32 (m and br respectively, 10 H, PPh_3), 7.22 (t, J = 7.7 Hz, 1 H, *p*-$C_6H_5PPh_2$), 6.99, 6.63 (t, J = 8 Hz, 2 H each, *o*- and *m*-$C_6H_5PPh_2$), 6.42 (m, 1 H, 4-pz$_{ax}$), 6.20 (t, 2 H, 4-pz$_{eq}$), 1.09, 0.96 (m, 2 H each, C_2H_4).

(25) Selected data for **5**: ^{1}H NMR (CD_2Cl_2, 250 K) 9.13 (s, 1 H, *H*Cpz$_3$), 8.66, 8.46, 7.51, 7.49, 7.13 (d, 1 H each, 3,5-pz), 7.41−7.30, 7.11, 7.00 (br, PPh_3), 6.35 (t, 1 H, 4-pz trans to H), 6.32 (m, 1 H, 4-pz trans to PPh_3), 4.94 (d, 1 H, 4-pz of cyclometalated arm), 3.87, 3.23 (m, 2 H each, C_2H_4), −17.14 (d, J_{PH} = 18.8 Hz, Ir*H*).

(26) At temperatures less than −10 °C, the isomerization of **4** to **5** is unreasonably slow. While isomerization occurs more readily at slightly higher temperatures, decomposition also becomes a more significant factor.

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(29) In this case, the pyrazolyl arm trans to the hydride ligand is displaced to form an equilibrium mixture of **7** and (η^2-Tp)Ir(PPh_3)$_2$(C_2H_4)H]BF_4 (K_{eq} = 30). Oldham, W. J.; Heinekey, D. M. Unpublished results.

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