polyphosphazene chemistry,[1] and studies on the synthesis and properties of analogues to **4**–**6** are in progress.

Acknowledgment. This work was carried out at The Pennsylvania State University. We thank the U.S. Army Research Office (H.R.A. and I.M.), Bayer AG, and the F.R.G. Ministry of Science and Technology (O.N. and G.R.) for financial support. We are also grateful to W. D. Coggio and K. Visscher for obtaining high field NMR spectra and DSC data, respectively.

A Hydridovinyliridium Complex More Stable Than Its η^2-Ethylene Isomer

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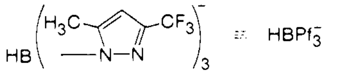
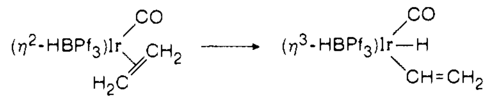
There is now strong evidence that η^2-benzene intermediates are involved in benzene activation to form complexes such as $(\eta$-$C_5Me_5)(Me_3P)Rh(H)(C_6H_5)$,[1] a possibility envisaged earlier.[2] It was thus natural to assume that an η^2 intermediate would be involved in the activation of olefinic C–H bonds by metal complexes. This notion was upset by the important observation that $(\eta$-$C_5Me_5)(Me_3P)Ir(\eta$-$C_2H_4)$ was more stable than its hydridovinyl isomer $(\eta$-$C_5Me_5)(Me_3P)Ir(H)(CH{=}CH_2)$ and thus could not be an intermediate in formation of the latter.[3] Other examples of this stability order, $L_nM(\eta^2$-$C_2H_4) > L_nM(H)(CH{=}CH_2)$, have been reported.[1b,4]

In experiments with an iridium complex of a new tris(pyrazolyl)borate ligand, we have encountered a particularly clear case in which this stability order is reversed. The new ligand is the tris(3-(trifluoromethyl)-5-methylpyrazol-1-yl)borato anion, designated $HBPf_3^-$ (**1**).[5] The complex is the four-coordinate, 16-electron $(\eta^2$-$HBPf_3)Ir(CO)(\eta^2$-$C_2H_4)$ (**2**).[7] The bidentate character of the $HBPf_3^-$ ligand in **2** follows from a systematic comparison of carbonyl stretching bands of related complexes and is similar to that found in $(\eta^2$-$HBPz^*_3)Rh(CO)(\eta^2$-olefin) (Pz* = 3,5-dimethylpyrazol-1-yl).[8] At 100 °C in cyclohexane in the dark, **2** goes completely to the hydridovinyl isomer **3**[9] as in eq 1.



1

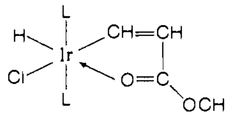
The half-life of the reaction is 4.5 h at 100 °C, and the only product besides **3** is a small amount (<5%) of $(HBPf_3)Ir(CO)_2$.



(1)

2 **3**

Recently, Werner et al.[10] have observed that a number of oxygenated vinyl derivatives such as methyl acrylate react with $Ir(Cl)\{P(i$-$Pr)_3\}_2$ to form an octahedral vinylic hydride **4**, {L = $P(i$-$Pr)_3$}, evidently via a less stable η^2-olefinic intermediate **5** {L = $P(i$-$Pr)_3$}. Stabilization of **4** relative to **5** was attributed to chelation of the carbonyl oxygen to iridium, resulting in an octahedral, 18-electron complex. The results we have described resemble Werner's, with the notable exception that the sixth ligand comes not from the olefin but from the tris(pyrazolyl)borate group. Isomerization of **2** to **3** amounts to intramolecular C–H activation, and the η^2 to η^3 change in the $HBPf_3^-$ ligand would stabilize the iridium(III) product. It was recently suggested that the intermolecular activation of benzene by $(\eta^2$-$HBPz^*_3)Rh(CO)(\eta^2$-olefin) was driven by a similar hapticity increase.[8]



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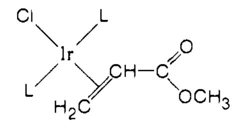
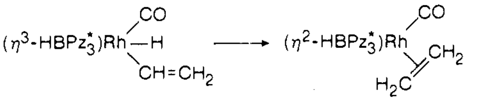


5

However, the possibility of achieving octahedral coordination is not a *sufficient* factor to stabilize the hydridovinyl form.[11] A cyclohexane solution of $(\eta^3$-$HBPz^*_3)Rh(CO)(H)(CH{=}CH_2)$, **6**,[12] isomerizes at 25 °C in the dark (half-life 3.2 min)[15] to the η^2-C_2H_4 complex **7**[8,16] (eq 2). The contrast in relative stabilities between compounds of the same general class that manifests itself in eq



(2)

6 **7**

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(1) (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240–4242. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663. (c) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620–631. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814–4819. (e) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91–100.

(2) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843–855. Giannotti, C.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1972**, 1114–1115. Parshall, G. W. *Catalysis* (*London*) **1977**, *1*, 335–368.

(3) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581–4582; **1988**, *110*, 5732–5744.

(4) (a) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856–4867. (b) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433–7434. (c) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7436–7438.

(5) $KHBPf_3$ was prepared by reaction of excess 3-(trifluoromethyl)-5-methylpyrazole[6] with KBH_4, slowly raising the temperature to 210 °C.

(6) Nishiwaki, T. *J. Chem. Soc. B* **1967**, 885–888.

(7) Data for **2**: pale yellow solid; IR (*n*-hexane) ν_{CO} 2030 cm^{-1}; ^1H NMR (CD_2Cl_2, ambient; although the spectrum is invariant to −80 °C, we think a fluxional process makes two of the pyrazole rings equivalent) δ 2.01 (m, 2 H, $CH_2{=}CH_2$), 2.40 (m, 2 H, $CH_2{=}CH_2$), 2.42 (s, 3 H, CH_3-Pf), 2.51 (s, 6 H, CH_3-Pf), 6.38 (s, 1 H, H-Pf), 6.51 (s, 2 H, H-Pf); ^{19}F NMR (CD_2Cl_2, $CFCl_3$ reference) δ −57.80 (s, 3 F), −60.40 (s, 6 F); MS (16 eV, 150 °C) 708 (32) M^+, 680 (100) $[M-CO \text{ or } C_2H_4]^+$, 652 (5) $[M-CO-C_2H_4]^+$. Anal. ($C_{18}H_{17}BF_9IrN_6O$) C, H, N.

(8) Ghosh, C. K.; Rodgers, D. P. S.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1988**, 1511–1512.

(9) Data for **3**: colorless, air-stable solid; IR (*n*-hexane) 2259 (w, br, ν_{Ir-H}), 2062 (s, ν_{CO}) cm^{-1}; ^1H NMR (CD_2Cl_2, ambient) δ −18.23 (s, 1 H, Ir–H), 2.48 (s, 3 H, CH_3–Pf), 2.50 (s, 3 H, CH_3-Pf), 2.55 (s, 3 H, CH_3–Pf), 5.17 (dd, 1 H, J = 18 Hz, 2 Hz, $CH{=}CH_2$), 5.84 (dd, 1 H, J = 10 Hz, 2 Hz, $CH{=}CH_2$), 6.43 (s, 1 H, H–Pf), 6.48 (s, 1 H, H–Pf), 6.52 (s, 1 H, H–Pf), 6.76 (dd, 1 H, J = 18 Hz, 10 Hz, $CH{=}CH_2$); MS (16 eV, 150 °C) 708 (26) M^+, 680 (100) $[M-CO \text{ or } C_2H_4]^+$. Anal. ($C_{18}H_{17}BF_9IrN_6O$) C, H, N.

(10) Werner, H.; Dirnberger, T.; Schulz, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 948–950. Both **4** and **5** were isolated, and thermal conversion of the methyl acrylate complex **5** to **4** was directly observed (Professor H. Werner, personal communication).

(11) We do not suggest that it is a *necessary* factor, even though it is a feature of the two categories presently known where the hydridovinyl isomer is more stable.

(12) Ultraviolet irradiation of $(HBPz^*_3)Rh(CO)_2$ in ethylene-purged cyclohexane at 25 °C produces the very labile[13] $(HBPz^*_3)Rh(CO)(H)(C_6H_{11})$, which reacts rapidly to form a mixture of **6** and **7**. Monitoring at 25 °C of the IR band of 6 at 2048 cm^{-1} established its first-order disappearance to form **7**. Complex 6 could not be isolated but was characterized as the chloro derivative after treating the mixture with CCl_4.[14]

(13) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726–4727.

(14) Data for $(HBPz^*_3)Rh(CO)(Cl)(CH{=}CH_2)$: pale yellow crystals; IR (*n*-hexane) ν_{CO} 2086 cm^{-1}; ^1H NMR (CD_2Cl_2, ambient, 200 MHz) δ 2.32 (s, 3 H, CH_3–Pz*), δ 2.38 (s, 3 H, CH_3–Pz*), δ 2.40 (s, 6 H, CH_3–Pz*, accidental degeneracy) 2.46 (s, 3 H, CH_3–Pz*), 2.52 (s, 3 H, CH_3–Pz*), 5.46 (d, 1 H, J = 16 Hz, $CH{=}CH_2$), 5.71 (d, 1 H, J = 7 Hz, $CH{=}CH_2$), 5.86 (s, 2 H, H–Pz*, accidental degeneracy), 5.88 (s, 1 H, H–Pz*), 7.03 (ddd, 1 H, J = 16 Hz, 7 Hz, $^2J_{Rh-H}$ = 3 Hz, $CH{=}CH_2$).

(15) If the isomerization is carried out with a 30-fold molar excess of benzene, no $(HBPz^*_3)Rh(CO)(H)(Ph)$[13] is formed. The latter is stable under these conditions, so it follows that the isomerization of 6 to **7** does not proceed by reductive elimination of ethylene followed by its recoordination. The reaction resembles in this way the isomerization of $(\eta$-$C_5Me_5)(Me_3P)Ir(H)(CH{=}CH_2)$ to $(\eta$-$C_5Me_5)(Me_3P)Ir(\eta^2$-$CH_2{=}CH_2)$,[3] although the rate in the iridium case is significant only above 180 °C.

(16) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 375–376.

1 and 2 is striking. An understanding would involve at a minimum some knowledge of metal-ligand bond strengths in complexes **2**, **3**, **6**, and **7**.

Most studies of C-H activation have focussed on aromatic and aliphatic hydrocarbons. In the equally important activation of olefins, the relative stability of $L_nM(H)(CH{=}CH_2)$ and $L_nM(\eta^2\text{-}C_2H_4)$ is a central question.

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Protonated Nitric Acid. Experimental Evidence for the Existence of Two Isomers

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Relatively little is known about the positive ion chemistry of HNO_3, e.g., its proton affinity (PA) is reported to be intermediate between those of H_2O and NH_3, which amounts to an uncertainty of almost 40 kcal mol^{-1}.[1] We have investigated by Fourier-transform (FT-ICR) and chemical ionization (CI) mass spectrometry, using H_3^+, CH_5^+, and H_3O^+ as the ionic reactants, the process

$$\mathrm{HNO_3 + AH^+ \rightarrow \underset{\mathbf{1}}{H_2NO_3^+} + A} \tag{1}$$

previously studied in a flowing afterglow.[2,3] Occurrence of reaction 1 has unequivocally been established by triple-resonance ICR experiments, demonstrating, in addition, slow decomposition of **1** into NO_2^+ and NO^+.[4] The CH_4/CI spectrum of aqueous HNO_3 displays **1** as the predominant peak, together with its hydrate, NO_2^+, and NO^+ (Figure 1).[5] Since the basicity of HNO_3 is hardly accessible to equilibrium measurements owing to the decomposition of **1** under ICR conditions, we resorted to the less reliable "bracketing" technique,[1] in experiments carried out either on isolated ions by FT-ICR spectrometry or by CIMS. The basicity of HNO_3 falls between those of H_2O and of CF_3COOH (or CF_3CH_2OH), leading to an estimated PA(HNO_3) = 168 ± 2 kcal mol^{-1}, not inconsistent with recent theoretical results.[6] From the PA value, one can derive ΔH_f° ($H_2NO_3^+$) ≈ 166 kcal mol^{-1}, hence $D(NO_2^+\text{-}H_2O) \approx 10$ kcal mol^{-1}, and $-\Delta H_{(1)} \approx 67$ (A = H_2), 36 (A = CH_4), and ≈ 2 (A = H_2O) kcal mol^{-1}.[1]

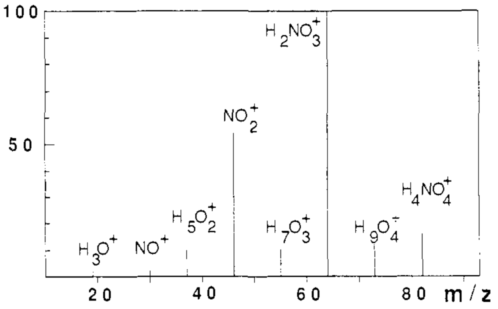

Figure 1. Typical CH_4/CI spectrum of 68% aqueous HNO_3, recorded at ca. 1 Torr, source temperature 40 °C, by using a 5982A Hewlett-Packard quadrupole spectrometer.

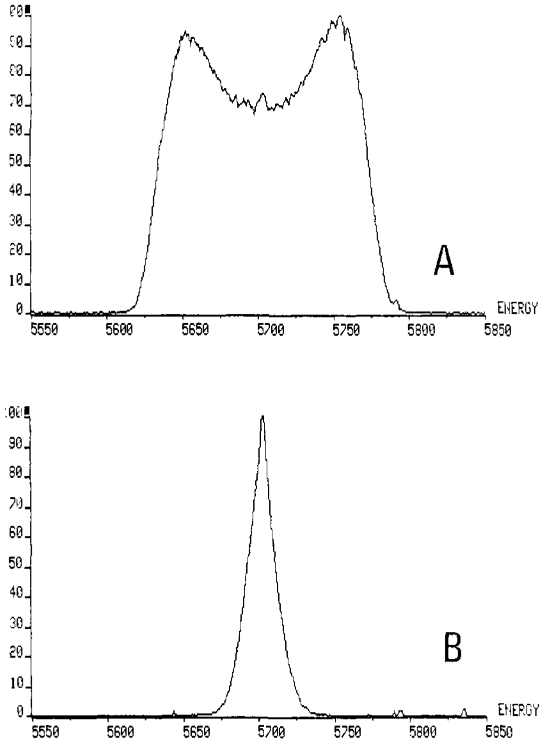

Figure 2. (A) Metastable peak due to the loss of water from ions of type II prepared according to process 1, A = CH_4, in methane at ca. 0.1 Torr. (B) Same peak from ions of type I, obtained by process 2, A = CH_4, in methane at ca. 1 Torr.

We have exploited as well another long-known[7] route to **1**:

$$\mathrm{C_2H_5ONO_2 + AH^+ \rightarrow H_2NO_3^+ + C_2H_4 + A} \tag{2}$$

a process exothermic by ca. 18 (A = CH_4) and 50 (A = H_2) kcal mol^{-1}.

Structurally diagnostic techniques provide strong and mutually supporting evidence for the existence of two isomers of **1**, isomer I being detectable in the ionic populations from reactions of low exothermicity, i.e., from (1), A = H_2O, and (2), A = CH_4, while isomer II is detectable only as a product from highly exothermic processes, i.e., from (1), A = H_2 or CH_4, and (2), A = H_2, under conditions of inefficient collisional deactivation.[8] Structural discrimination between I and II is based on the following evidence.

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[1] All thermochemical data are taken from the compilation of Lias et al. (Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695).

[2] Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1973**, *59*, 6272.

[3] Fehsenfeld, F. C.; Howard, C. J.; Schmeltekopf, A. L. *J. Chem. Phys.* **1975**, *63*, 2835.

[4] The ICR spectra were recorded with a Nicolet FTMS 1000 instrument, measuring the sample pressure with a Granville-Phillips 280 Bayard-Alpert ion gauge, at a typical resolution of 10^3 fwhh at mass 100, with a trapping voltage of 1.0 V, electron-beam energy 15 eV, under a total pressure of ca. 4×10^{-7} Torr.

[5] $H^+(HNO_3)_x(H_2O)_y$ clusters have been reported, see: Kay, B. D.; Hermann, V.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1981**, *80*, 469 and references therein.

[6] According to 6-31G**//44-31G SCF calculations by Nguyen et al. (Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1984**, 2043), the PA of HNO_3 exceeds that of H_2O by ca. 1 kcal mol^{-1}. Such results, while internally consistent, overestimate absolute basicities, e.g., the calculated PA(H_2O) exceeds the experimental value by some 13 kcal mol^{-1}, which could affect the calculated $D(NO_2^+\text{-}H_2O)$ energy.

[7] Nixon, W. B.; Bursey, M. M. *Tetrahedron* **1970**, *50*, 4389.

[8] These observations do not imply that II is the only or the most abundant isomer formed whenever the protonation process is highly exothermic but simply that only under the specified set of conditions it becomes detectable by MIKE and CID spectrometry. Such structurally diagnostic techniques detect the fraction of the ions that undergo unimolecular or collisionally induced decomposition in the appropriate regions of the spectrometer, rather than sampling the relative ionic abundances in the ion source.

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