Theoretical Studies of Inorganic and Organometallic Reaction Mechanisms. 10. Reversal in Stability of Rhodium and Iridium η^2-Ethene and Hydridovinyl Complexes

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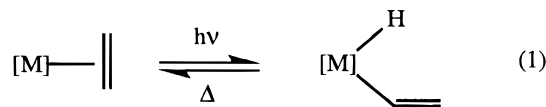
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Ab initio quantum mechanical calculations were used to examine models for the reaction $[\eta^3\text{-HB(X)}_3](CO)M(\eta^2\text{-CH}_2CH_2) \rightarrow [\eta^2\text{-HB(X)}_3](CO)M(\eta^2\text{-CH}_2CH_2) \rightarrow [\eta^3\text{-HB(X)}_3](CO)M(H)$-$(CHCH_2)$, for which it is known that the equilibrium lies toward the hydridovinyl product for iridium, with X = 3-trifluoromethyl-5-methylpyrazol-1-yl, and lies toward the η^2-ethene reactant for rhodium, with X = 3,5-dimethylpyrazol-1-yl, and most other related systems. The ligand models tested correspond to X = $NHNH_2$, $NHNCHF$, $N_2C_3H_3$ (pyrazol-1-yl), $N_2C_3H_2F$ (3-fluoropyrazol-1-yl), $N_2C_3H_2F$ (5-fluoropyrazol-1-yl), $N_2C_3H_2CH_3$ (3-methylpyrazol-1-yl), and $N_2C_3H_2CF_3$ (3-(trifluoromethyl)pyrazol-1-yl). For the iridium complexes, the restricted Hartree−Fock (RHF) optimized geometries are similar to the Møller−Plesset second-order (MP2) ones and the energy calculations at the MP2//RHF, MP2//MP2, and MP4SDQ//MP2 levels give reasonable results. For the rhodium complexes, although the RHF energies appear to be in qualitative accord with the calculated results at the MP2//MP2 and MP4SDQ//MP2 levels, the MP2//RHF energies are not in agreement with these results since the RHF geometries of $(\eta^3\text{-HBX}_3)(\eta^2\text{-ethene})$rhodium complexes are very sensitive to the electronic environment. In the d^8 η^2-ethene complexes, Rh favors η^2-pyrazolylborate over η^3-pyrazolylborate complexes by −0.7 to −9.9 kcal/mol and the barrier from the hydridovinyl complex is only 12 kcal/mol. Thus, nearly all Rh complexes will exist as $(\eta^2\text{-ethene})(\eta^2\text{-pyrazolylborate})$ complexes. In contrast, Ir favors the η^3-pyrazolylborate over η^2-pyrazolylborate in all complexes and endothermicty to the hydridovinyl complex is reduced by about 20 kcal/mol. The ethene complexes are the most sensitive to the steric properties of the pyrazolylborate ligands. Thus, in the most sterically hindered Ir complexes, the hydridovinyl complex finally becomes more stable than its η^2-ethene isomer.

Introduction

The relative stability between ethylene complexes, $L_nM(\eta^2\text{-CH}_2CH_2)$, and their hydridovinyl isomers, L_nM-$(H)(CHCH_2)$, has been subject to many studies in the past 10 years.[1,2] The interest in this field has been stimulated by questions about the mechanism of C−H bond activation in unsaturated transition metal complexes; specifically, whether η^2-intermediates are involved in reactions such as benzene activation in the formation of $(Cp^*)(Me_3P)Rh(H)(C_6H_5)$,[3] where $Cp^* = \eta^5$-C_5Me_5. Compared with the η^2-ethene π-complexes, the metal vinyl hydride complexes are usually thermally unstable (reaction 1).[1i,j] However, in the case of reaction 2 Ghosh et al.[1a,b] showed that the hydridovinyl isomer (**2**) is favored over the η^2-ethene isomer (**1**) in this pyrazolylborate iridium system. According to Ghosh et al., reaction 2 proceeds with a half-life of 4.5 h at 100 °C in the dark and the only product besides **2** is a small amount (<5%) of $(HBPf_3)Ir(CO)_2$.[1a] It is clearly different from an analogous pyrazolylborate rhodium system, in which the η^2-ethene complex (**4**) is produced from the hydridovinyl complex (**3**) at 25 °C in the dark with a half-life of 3.2 min, as shown in reaction 3.[1b]

To our knowledge, only a few theoretical studies on the ethylene/hydridovinyl interconversion have been performed and none of them have included pyrazolylborate ligands. Silvestre et al.[2a] studied the interconversion on the unsaturated complex $(Cp)(PH_3)Ir$ at the extended-Hückel level. They also found an η^2-ethene complex in the reaction slightly more stable and more

$$[M]\text{---}\| \; \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \; [M]\diagup\diagdown \qquad (1)$$

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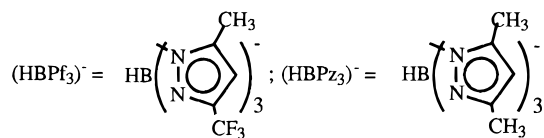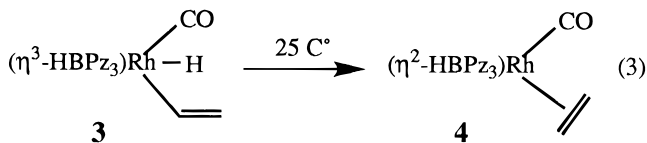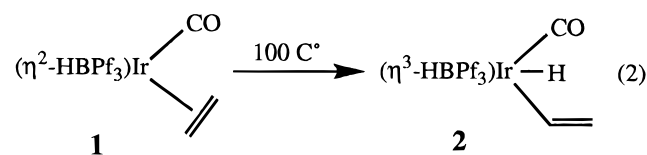
sensitive to the steric effects of a Cp ring and phosphine than the hydridovinyl isomer. Siegbahn et al.[2b] studied the interconversion on bare second-row transition metal atoms, with geometries at the restricted Hartree–Fock (RHF) level, energies at the modified coupled pair functional (MCPF) level, and corrections estimated at the CCSD(T) level (coupled cluster singles and doubles plus a perturbational estimate of the triples). They found that the η^2-ethene isomer is thermodynamically favored for all but the zirconium ($\Delta E = -1.2$ kcal/mol) atom.

In this work, we report our search for suitable models for reactions 2 and 3 in particular, model ligands for the pyrazolylborates, and our examination of the level of calculation suitable for the comparison between rhodium and iridium. The model reactions are represented by Scheme 1 with M = Rh (**5**, **6**, and **7**) and Ir (**8**, **9**, and **10**). The complexes **5**, **7**, **8**, and **10** are η^3-pyrazolylborate structures and **6** and **9** are η^2-pyrazolylborate structures.

Theoretical Details

The geometries of the model compounds shown in Scheme 1 were optimized initially at the restricted Hartree–Fock[4] (RHF) level. The ligands $NHNH_2$ and $NHNCHF$ were held planar, since they were modeling the pyrazol-1-yl rings in real systems. Energies were calculated at the second-order Møller–Plesset[5] (MP2) level using RHF optimized geometries. For the compounds with X = $NHNH_2$ and $NHNCHF$, the geometries were also optimized at the MP2 level and the energies at the third-order Møller–Plesset (MP3)[5] level and fourth-order Møller–Plesset level with single, double, and quadruple substitutions (MP4SDQ)[5c] were also calculated at the MP2 geometries. The transition states (TS) were determined by a Quasi-Newton method,[6] in which the final updated Hessian shows only one negative eigenvalue.

Effective core potentials were used for all atoms but hydrogen. For rhodium and iridium, the $(n-1)s$ and $(n-1)p$ electrons were taken as active and the core potentials and basis sets were those of Hay and Wadt.[7a] In this work, the Ir (55,5,3) and Rh (55,5,4) basis sets of Hay and Wadt were split to obtain Ir (541,311,21) and Rh (541,311,31) basis sets. For

B, C, N, O, and F, the double-ζ basis sets and effective core potentials of Stevens et al.[7b] were used. For hydrogen, the Dunning–Huzinaga[7c] double-ζ basis was used. In one test case, for the reaction energy of **8a** → **10a**, we used a somewhat larger basis set[8] for Ir and added polarization functions[9] to the CO, ethane, and hydridovinyl ligands. This change in basis set caused the endothermicity of the reaction to increase by 4.4 kcal/mol at the MP2//RHF level.

The energies reported in this work correspond to the electronic and nuclear-repulsion contributions to the internal energy with the Born–Oppenheimer approximation. To obtain ideal gas enthalpy changes of our reactions, one would need to include the transitional, rotational, and vibrational contributions to the internal energy plus PV ($H = E + PV$) for each component. For our model reactions, which may be called isomerizations, many of these additional energy contributions cancel and the only significant additional term at room temperature is the vibrational energy change at 0 K (zero point contribution). Since the relative positions of most of the atoms in our model reactions are almost unchanged (replacement of a weak M–ethene bond by a stronger M–C bond and a strong C–H bond by a weaker M–H bond), the zero point energy (ZPE) change will be small. We estimate the zero-point contribution to be about ±4 kcal/mol. As a check of this estimate, we performed a ZPE calculation for the transformation $H_2Ti(CHCH_2)(H) \rightarrow H_2Ti(\eta^2\text{-}CH_2\text{=}CH_2)$ and found the ZPE correction to be 2.6 kcal/mol.

All ab initio calculations were performed with GAMESS-UK,[9a] Gaussian92, and Gaussian94 programs[9b] at the Cornell Theory Center on an IBM ES6000 and Scalable Powerparallel, at the Department of Chemistry and the Supercomputer Center of Texas A&M University on Silicon Graphics Power Challenge servers, and on Silicon Graphics Indigo I and Power Indigo II workstations in our laboratory and at the Institute of Scientific Computation of Texas A&M University.

Results and Discussion

Electronic Effect and Isomerization Energy. To obtain reasonable structures and relative energies, we have carried out both RHF and MP2 geometry optimizations for the model compounds **5a**,**b**, **7a**,**b**, **8a**,**b**, and **10a**,**b**. The optimized geometries of the rhodium and iridium complexes are shown in Figures 1 and 2, respectively. For iridium, the RHF optimized geometries are very similar to the MP2 optimized ones. The RHF and MP2 optimized distances of the Ir–N, Ir–C (ethylene), and Ir–C (vinyl) bonds are in very good agreement with the experimental values.[1c,10] The largest changes from RHF to MP2 geometries occur for the Ir–CO, C≡O, and C=C bond lengths. The Ir–CO bonds at the MP2 level are shorter by 0.07–0.08 Å than at the RHF level. The C≡O and C=C bonds at the MP2 level are longer by 0.04–0.08 Å with respect to those at the RHF level. It is clear that the back-donating interaction between Ir and CO and between Ir and

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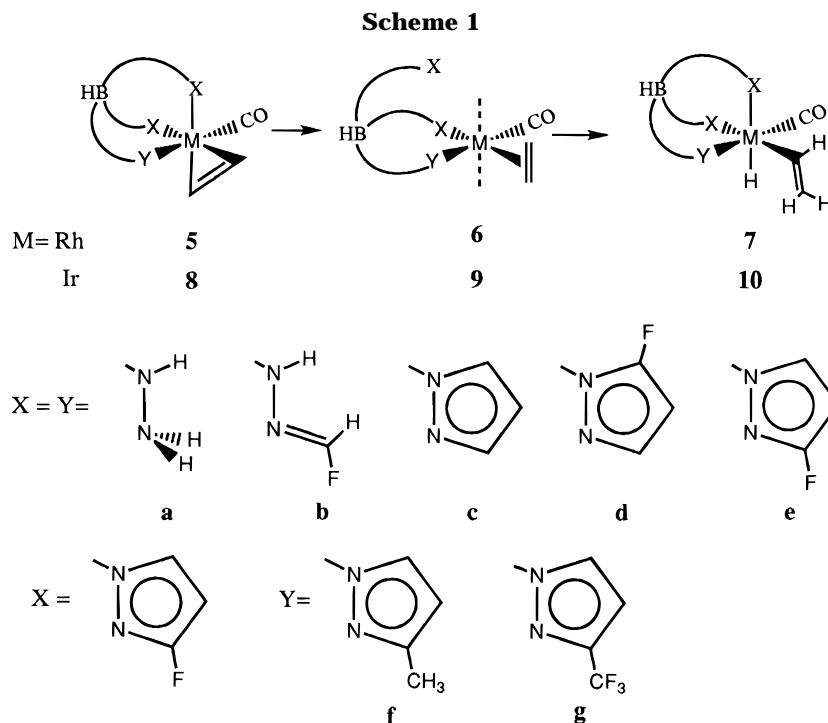(10) (a) Bovens, M.; Gerfin, T.; Gramlich, V.; Petter, W.; Venanzi, L. M.; Haward, M. T.; Jackson, S. A.; Eisenstein, O. *New J. Chem. (Nouv. J. Chim.)* **1992**, *16*, 337. (b) Fernandez, M. J.; Rodriguez, M. J.; Oro, L. A.; Lahoz, F. J. *J. Chem. Soc., Dalton Trans.* **1989**, 2073. (c) Cleary, B. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1995**, *117*, 3510.

Scheme 1

ethylene at the MP2 level is much stronger than that at the RHF level. In comparison to the experimental values of the Ir−CO (1.880 Å), C≡O (1.145 Å), and C=C (1.42 Å) bonds,[10c] the MP2 calculations overestimate the degree of back-donation interactions because the back-bonding interactions involves two closely spaced orbitals on the metal and ligand.[11] The change of nucleophilicity from model **a** to **b** only results in a slight geometrical change of **8** and **10** at both the RHF and MP2 levels. For rhodium, the RHF optimized geometries of **5a**, **7a**, and **7b** are very similar to the MP2 optimized ones. Again, the largest changes from RHF to MP2 geometries occur for the Rh−CO, C≡O, and C=C bond lengths since the MP2 calculations again overestimate the back-donating interactions between Rh and CO and between Rh and ethylene. At variance with these general observations is the structure of **5b**, in which the largest change from the RHF to MP2 geometry appears in the Rh−C (ethylene) (−0.17 Å), Rh−N (−0.4 and −0.23 Å), and C=C (+0.12 Å) bonds lengths. This large difference between the RHF and MP2 geometries is similar to the results for a different rhodium system reported by us in previous work.[12] There is also an unexpectedly large difference between the structure of **5b** and that of **5a**; in particular, the Rh−C (ethylene) bond of **5b** is longer by 0.14 Å than that of **5a** at the RHF level. Compared to **7**, **8**, and **10**, the RHF geometries of the rhodium η^2-ethene complexes, **5**, are very sensitive to the change of nucleophilicity from model **a** to **b**. The weaker nucleophilicity of **b** results in an underestimation of the back-donating interactions between Rh and CO and between Rh and ethylene in the rhodium η^2-ethene complexes at the RHF level. This deficiency affects the geometry optimizations at the RHF level but shows

an even larger effect on the energy calculations at higher levels such as MP2, when RHF geometries are used.

The relative energy between the metal η^2-ethene, **5a,b** and **8a,b**, and hydridovinyl complexes, **7a,b** and **10a,b**, calculated at the RHF//RHF, MP2//RHF, MP2//MP2, MP3//MP2, and MP4SDQ//MP2 levels are shown in Table 1. For M = Ir, the energy differences between **10a** and **8a** and between **10b** and **8b** are very small at the RHF//RHF and MP3//MP2 levels. However, at the MP2//RHF level, the reactions from **8** to **10** with X = NHNH₂ (**a**) and NHNCHF (**b**) become endothermic by 7.5 and 6.4 kcal/mol, respectively, in good agreement with the values calculated at the MP2//MP2 and MP4SDQ//MP2 levels. Thus, an increase of the nucleophilicity of the hydrazonlylborate ligand only results in a small change of the relative energy between the iridium η^2-ethene and hydridovinyl complexes. For M = Rh, the largest difference in the reaction energy occurs between the MP2//RHF and MP2//MP2 levels for the reaction **5b → 7b**, because of the previously noted large change from RHF to MP2 geometries. The small isomerization energy of 0.18 kcal/mol at the MP2//RHF level is contrary to the experimental results. Thus, the geometry optimizations of **5b** at the RHF level are incompatible with the energy calculation at the MP2 level. Even so, the RHF//RHF relative energies, 17.0−28.5 kcal/mol, are qualitatively in concert with those of the MP2//MP2 and MP4SDQ//MP2 levels, 14.6−20.0 kcal/mol, which are in good agreement with the matrix experimental results. Thus, for the Rh complexes, the RHF//RHF energy values will be somewhat more accurate with respect to the trends, because they are internally consistent, whereas the MP2//RHF results will show capricious variations.

The isomerizations of the rhodium η^2-ethene complex to the rhodium hydridovinyl complex with X = NHNH₂ (**a**) and NHNCHF (**b**) are more endothermic by 11.4−13.6 kcal/mol than those of the iridium complexes at the MP2//MP2 and MP4SDQ//MP2 levels. In comparison

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	RHF	MP2
5a		
Rh-N(eq)	2.360	2.262
	2.148	2.157
Rh-N(ax)	2.362	2.262
Rh-CO	2.006	1.816
Rh-C	2.177	2.155
Rh-H	–	–
C≡O	1.143	1.223
C=C	1.429	1.508
8a		
Ir-N(eq)	2.272	2.247
	2.165	2.180
Ir-N(ax)	2.273	2.247
Ir-CO	1.900	1.825
Ir-C	2.124	2.154
Ir-H	–	–
C≡O	1.153	1.232
C=C	1.485	1.523

	RHF	MP2
7a		
Rh-N(eq)	2.244	2.238
	2.114	2.153
Rh-N(ax)	2.274	2.243
Rh-CO	2.022	1.844
Rh-C	2.064	2.063
Rh-H	1.569	1.595
C≡O	1.139	1.214
C=C	1.359	1.392
10a		
Ir-N(eq)	2.228	2.223
	2.147	2.169
Ir-N(ax)	2.245	2.222
Ir-CO	1.918	1.840
Ir-C	2.079	2.076
Ir-H	1.604	1.618
C≡O	1.148	1.224
C=C	1.359	1.395

Figure 1. RHF and MP2 optimized geometries of the rhodium and iridium complexes, **5a**−**10a**.

	RHF	MP2
5b		
Rh-N(eq)	2.478	2.250
	2.248	2.215
Rh-N(ax)	2.478	2.250
Rh-CO	2.031	1.814
Rh-C	2.319	2.147
Rh-H	–	–
C≡O	1.139	1.212
C=C	1.388	1.507
8b		
Ir-N(eq)	2.319	2.220
	2.242	2.216
Ir-N(ax)	2.319	2.220
Ir-CO	1.907	1.825
Ir-C	2.131	2.160
Ir-H	–	–
C≡O	1.147	1.220
C=C	1.467	1.517

	RHF	MP2
7b		
Rh-N(eq)	2.300	2.243
	2.158	2.158
Rh-N(ax)	2.342	2.257
Rh-CO	2.021	1.853
Rh-C	2.041	2.060
Rh-H	1.534	1.580
C≡O	1.136	1.205
C=C	1.352	1.385
10b		
Ir-N(eq)	2.253	2.207
	2.162	2.153
Ir-N(ax)	2.287	2.215
Ir-CO	1.931	1.847
Ir-C	2.068	2.073
Ir-H	1.576	1.604
C≡O	1.142	1.213
C=C	1.353	1.389

Figure 2. RHF and MP2 optimized geometries of the rhodium and iridium complexes, **5b**−**10b**.

of **5b** → **7b** with **5a** → **7a**, the MP2//MP2 and MP4SDQ//MP2 results suggest that the change of the nucleophilicity of the pyrazolylborate ligand has a slightly greater influence on the isomerization energy for the rhodium compounds.

C−H Bond Activation Processes of Ethylene by Pyrazolylborate Complexes.

The C−H bond activation of ethylene in the pyrazolylborate transition metal complexes may be involved in two possible reaction routes as shown in Scheme 2. The first route indicates that the η^3-pyrazolylborate vinyl hydride complex may form directly from the η^3-pyrazolylborate η^2-ethene complex; the second route shows that the C−H bond-activation process may involve formation of an η^2-pyrazolylborate η^2-ethene intermediate before the activation step.

To understand this isomerization process, we have examined the model reactions with X = NHNCHF (**b**) for M = Rh and Ir, which are similar to the real pyrazolylborate system because the ligand HB-(NHNCHF)$_3$ includes both a π system and F. The RHF-optimized geometries of the η^2-hydrazonylborate intermediates (**6b** and **9b**) and transition states (**TS**$_{6-7}$ and **TS**$_{9-10}$) are given in Figure 3. It is clear that the η^2-

Table 1. Relative Energies (kcal/mol) between the Metal η^2-Ethene, 5a,b and 8a,b, and Hydridovinyl Complexes, 7a,b and 10a,b, at the RHF//RHF, MP2//RHF, MP2//MP2, MP3//MP2, and MP4SDQ Levels

	Rh		Ir		Rh		Ir	
	5a	7a	8a	10a	5b	7b	8b	10b
RHF//RHF	0.00	16.99	0.00	−0.58	0.00	28.45	0.00	2.32
MP2//RHF	0.00	14.57	0.00	7.53	0.00	0.18	0.00	6.40
MP2//MP2	0.00	20.00	0.00	7.60	0.00	19.20	0.00	7.83
MP3//MP2	0.00	11.15	0.00	0.31	0.00	12.77	0.00	0.25
MP4SDQ//MP2	0.00	18.80	0.00	5.32	0.00	19.13	0.00	5.48

hydrazonylborate η^2-ethene complexes, **6** and **9**, adopt square planar structures, which are very different from the octahedral structures of the η^3-hydrazonylborate η^2-ethene complexes, **5** and **8**. The largest changes from the η^3-hydrazonylborate η^2-ethene complexes to the η^2-hydrazonylborate η^2-ethene complexes, apart from the leaving donor, occur for the distances of the M−C (ethylene) bonds (+0.11 to +0.12 Å), M−N$_{eq}$ bonds (−0.09 to −0.29 Å), and C=C bond (−0.02 to −0.06 Å). Thus, the η^3-hydrazonylborate η^2-ethene complexes, **5** and **8**, are closer to M(III) d^6 complexes, "metallocyclopropane" ligands, while the η^2-hydrazonylborate η^2-
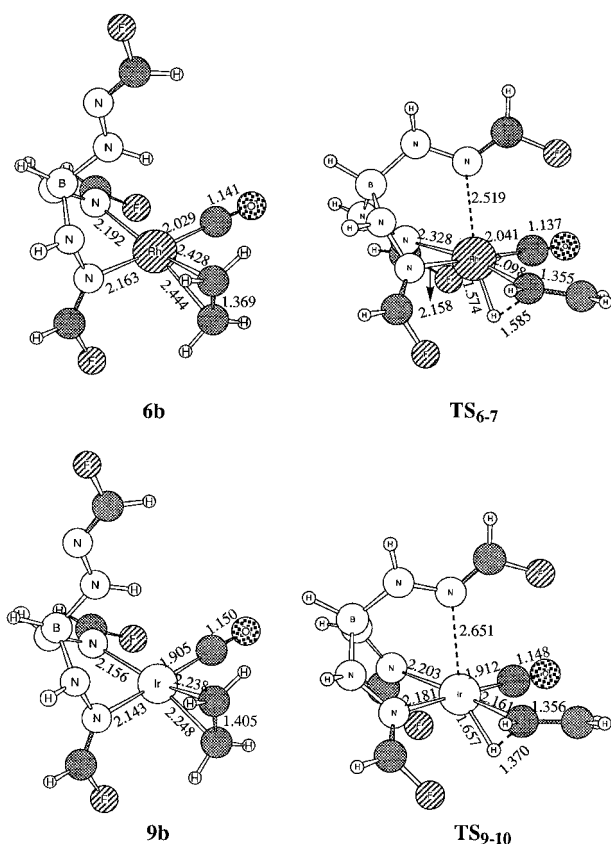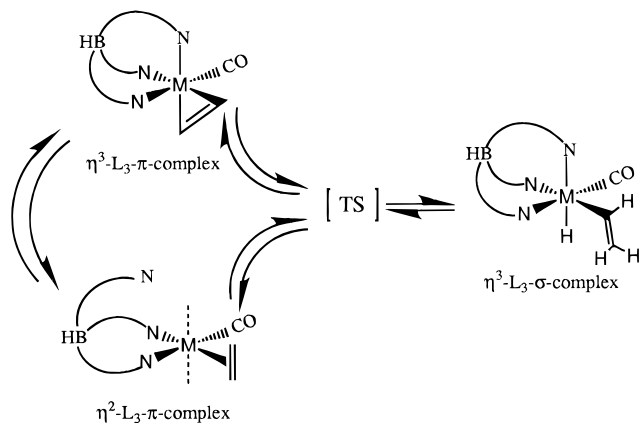
Figure 3. RHF optimized geometries of the rhodium and iridium complexes, **6b** and **9b**, and transition states, **TS$_{6-7}$** and TS$_{9-10}$.

Scheme 2

ethene complexes, **6** and **9**, more closely resemble M(I) d^8 ethylene complexes. Despite careful searches for the transition states along both possible reaction pathways, we found only one transition state, **TS$_{6-7}$** for Rh and **TS$_{9-10}$** for Ir, respectively, in which the M–N$_{ax}$ distances are longer by 0.04–0.36 Å than those of the η^3-hydrazonylborate η^2-ethene complexes. Comparing **TS$_{6-7}$** with **TS$_{9-10}$**, the transition state of the rhodium complex is much later than that of the iridium complex, as one would expect from its greater endothermicty.

The energy profiles for the isomerizations of the rhodium and iridium η^3-pyrazolylborate η^2-ethene complexes through the η^2-pyrazolylborate η^2-ethene complexes to the hydridovinyl complexes are shown in Figures 4 and 5. For M = Rh (Figure 4), **6b** is slightly less stable by 1.9 kcal/mol than **5b** and more stable by 26.6 kcal/mol than **7b**, at the RHF level. The C–H

activation barrier of **6b** → **7b** is calculated to be 38.7 kcal/mol at the RHF level, an indication of a very unfavorable process. In contrast, the low barrier (12.1 kcal/mol) and large exothermicity (26.6 kcal/mol) of the reverse reaction, **7b** → **6b**, indicate that isomerization of the rhodium hydridovinyl complexes to the η^2-ethene complexes should be thermodynamically favored, in agreement with the experimental results. For M = Ir (Figure 5), **9b** is less stable by 19.1 kcal/mol than **8b** and by 12.7 kcal/mol than **10b** at the MP2//RHF level. The C–H activation barrier of **9b** → **10b** is calculated to be 24.6 kcal/mol at the MP2//RHF level. Compared to the experimental barrier for the thermal conversion of CpIr(L)(CHCH$_2$)(H) to CpIr(L)(η^2-CH$_2$CH$_2$) (L = CO, PR$_3$, and ethylene) (17–32 kcal/mol),[1h] the MP2//RHF calculated barrier is reasonable. It is clear that this process could occur at reasonable temperatures and that the equilibrium direction will depend on the relative stability of **8** and **10**. Thus, it is essential to investigate further the relative stability between the η^2-ethene and hydridovinyl complexes of other model ligands, as this reaction **8** → **10** is experimentally exothermic for at least some ligands.

Steric Effect and Isomerization Energy. To elucidate the influences of the possible electronic and steric effects on the isomerization of the rhodium and iridium η^2-ethene complexes to hydridovinyl complexes, the geometries of a series of pyrazolylborate complexes, **5–10** with the ligands **c–g**, were optimized at the RHF level. The optimized geometrical parameters are summarized in Table 2 for M = Rh and in Table 3 for M = Ir. For M = Ir, the changes in the ligands' electronic and steric properties have only slight influences on the geometries of **9c–g** and **10c–g**. However, with the increased steric bulk of the ligand in **8**, the Ir–C (ethylene) bond length increases and the C=C bond length decreases. Thus, the steric effects of the pyrazolylborate ligands are transmitted most strongly to the strength of the M–C (ethylene) bond in the η^2-ethene complexes, **8**, which could lead to an increasing instability of the iridium η^2-ethene complexes, **8**, relative to the hydridovinyl complexes, **10**. Similar patterns are seen for the Rh complexes, even though the absolute accuracy of these RHF geometries are poorer than those for Ir.[13]

The relative energies for the isomerization of the rhodium and iridium η^2-ethene to hydridovinyl complexes at the RHF//RHF and MP2//RHF levels are shown in Table 4. As we have shown earlier, the MP2//RHF energies cannot be trusted for Rh and they are given here only for completeness. Although the RHF//RHF energies for the Rh complexes are not particularly accurate, they are generally consistent with higher level calculations (MP2//MP2). Thus, we believe we can get a general, if somewhat vague, idea of the trends for the Rh complexes with differing ligands from the RHF//RHF results. For the Ir complexes, we would expect to find similar trends for the RHF//RHF and MP2//RHF results with the change in energy for the MP2 to be a slight overestimation. For the rhodium complexes, the results show (i) that all rhodium complexes favor the η^2-pyrazolylborate η^2-ethene structure and (ii) that the all rhodium hydridovinyl complexes are thermally unstable by 20–28 kcal/mol with respect to the η^2-pyrazolylborate η^2-ethene complexes at the RHF//RHF level, in very
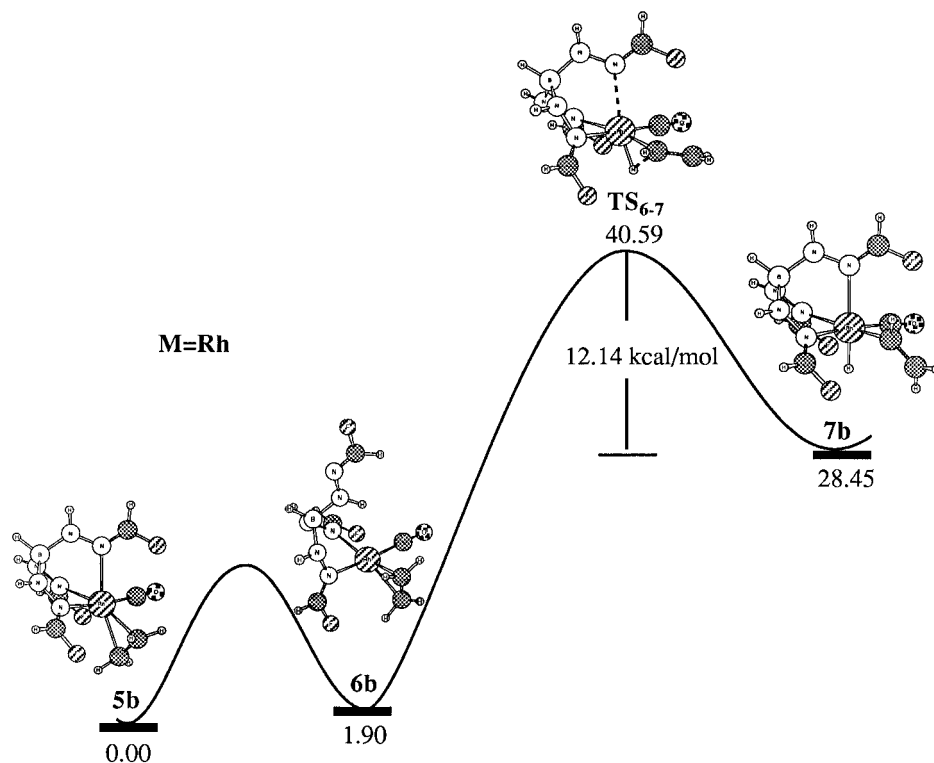
Figure 4. Profile of the potential energy surfaces at the MP2//RHF level for **5b** → **7b**. Both **5b** and **6b** can be reached directly from **TS$_{6-7}$** as shown in Scheme 2.
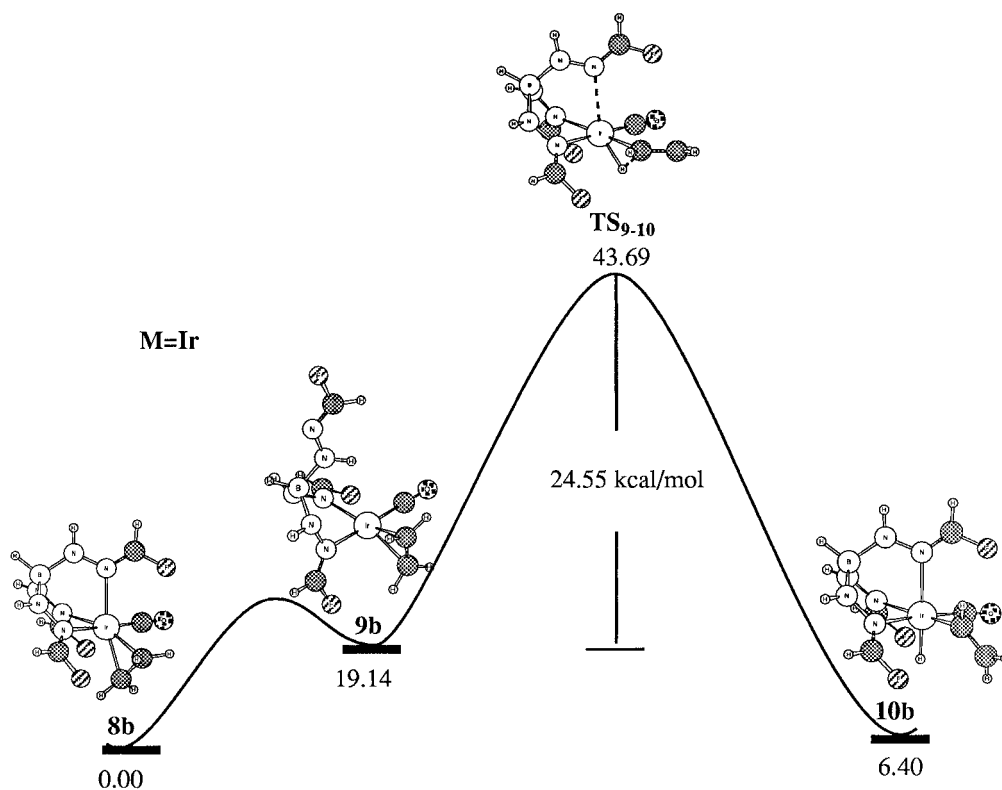

Figure 5. Profile of the potential energy surfaces at the RHF//RHF level for **8b** → **10b**. Both **8b** and **9b** can proceed directly to the same transition state (**TS$_{9-10}$**) as shown in Scheme 2.

good agreement with the experimental results. The iridium complexes appear very different from the rhodium ones: (i) all iridium η^2-pyrazolylborate η^2-ethene complexes are thermally unstable with respect to the η^3-pyrazolylborate η^2-ethene complexes at the MP2//RHF level, a result in disagreement with the results expected by Ghosh et al.; (ii) the relative stability of the

iridium hydridovinyl complexes with respect to the η^3-pyrazolylborate η^2-ethene complexes clearly depends on the steric effect of the pyrazolyl group. Strong steric effects result in an increase in the relative stability of the iridium hydridovinyl complexes. Thus, when the ligand is the tris(3-(trifluoromethyl)-5-methylpyrazol-1-yl)borato anion (model **g**), the isomerization of the

Table 2. Bond Distances (Å) for 5, 6, and 7 with the Model Ligands c−g for M = Rh

	Rh−N$_{(eq)}$	Rh−N$_{(ax)}$	Rh−CO	Rh−C	Rh−H	C≡O	C=C
	Ligand **c**						
5	2.239	2.344	2.000	2.189		1.143	1.419
6	2.146	3.115	1.992	2.424		1.146	1.370
7	2.147	2.241	2.009	2.052	1.556	1.139	1.358
	Ligand **d**						
5	2.242	2.347	2.003	2.195		1.142	1.417
7	2.148	2.242	2.010	2.051	1.555	1.138	1.358
	Ligand **e**						
5	2.284	2.392	2.012	2.254		1.141	1.400
6	2.169	3.096	2.010	2.452		1.143	1.368
7	2.171	2.270	2.011	2.045	1.544	1.137	1.354
	Ligand **f**						
5	2.362	2.382	2.000	2.225		1.140	1.406
6	2.162	3.088	2.011	2.482		1.144	1.366
7	2.166	2.262	2.021	2.047	1.547	1.137	1.355
	Ligand **g**						
5	2.362	2.382	2.002	2.277		1.140	1.396
6	2.187	3.061	2.013	2.497		1.143	1.365
7	2.190	2.273	2.005	2.044	1.538	1.136	1.353

Table 3. Bond Distances (Å) for 8, 9, and 10 with the Model Ligands c−g for M = Ir

	Ir−N(eq)	Ir−N$_{(ax)}$	Ir−CO	Ir−C	Ir−H	C≡O	C=C
	Ligand **c**						
8	2.182	2.226	1.895	2.117		1.153	1.482
9	*a*						
10	2.140	2.203	1.915	2.073	1.595	1.148	1.359
	Ligand **d**						
8	2.183	2.227	1.896	2.118		1.152	1.481
10	2.141	2.204	1.917	2.072	1.593	1.147	1.358
	Ligand **e**						
8	2.213	2.250	1.900	2.126		1.149	1.472
9	2.135	3.958	1.894	2.258		1.153	1.402
10	2.158	2.225	1.922	2.070	1.585	1.144	1.355
	Ligand **f**						
8	2.222	2.235	1.900	2.117		1.149	1.479
9	2.131	3.318	1.894	2.245		1.154	1.404
10	2.156	2.220	1.927	2.070	1.587	1.144	1.356
	Ligand **g**						
8	2.280	2.240	1.887	2.127		1.149	1.471
9	2.149	3.892	1.892	2.272		1.153	1.400
10	2.174	2.228	1.919	2.068	1.580	1.144	1.354

a No minimum is found.

iridium η^3-pyrazolylborate η^2-ethene complexes to hydridovinyl complexes becomes exothermic, −6.28 and −0.82 kcal/mol at the RHF//RHF and MP2//RHF levels, respectively, in very good agreement with the experimental result of Ghosh et al.[1a,b]

Conclusions

Seven different models for the isomerization of the rhodium and iridium η^2-ethene to hydridovinyl complexes, $[\eta^3$-HB(X)$_3](CO)M(\eta^2$-CH$_2$CH$_2) \rightarrow [\eta^2$-HB(X)$_3]$-(CO)M(η^2-CH$_2$CH$_2) \rightarrow [\eta^3$-HB(X)$_3](CO)M(H)(CHCH$_2$), were studied, with X = NHNH$_2$, NHNCHF, N$_2$C$_3$H$_3$ (pyrazol-1-yl), N$_2$C$_3$H$_2$F (3-fluoropyrazol-1-yl), N$_2$C$_3$H$_2$F

Table 4. Relative Energies (kcal/mol) of the Isomerization of 5 → 7 and 8 → 10

		Rh			Ir		
X		5	6	7	8	9	10
c	RHF//RHF	0.00	−0.72	18.98	0.00		−0.29
	MP2//RHF	0.00	21.32	13.45	0.00		8.89
d	RHF//RHF	0.00		19.79	0.00		0.15
	MP2//RHF	0.00		13.27	0.00		9.22
e	RHF//RHF	0.00	−2.98	25.31	0.00	6.93	2.60
	MP2//RHF	0.00	−13.64	8.72	0.00	21.12	9.78
f	RHF//RHF	0.00	−5.79	16.16	0.00	6.58	−5.37
	MP2//RHF	0.00	10.98	0.59	0.00	18.27	1.69
g	RHF//RHF	0.00	−9.93	18.21	0.00	−0.70	−6.28
	MP2//RHF	0.00	4.32	−3.84	0.00	12.57	−0.82

(5-fluoropyrazol-1-yl), N$_2$C$_3$H$_2$CH$_3$ (3-methylpyrazol-1-yl), and N$_2$C$_3$H$_2$CF$_3$ (3-(trifluoromethyl)pyrazol-1-yl). Our calculations show that the RHF geometries of the rhodium η^2-ethene complexes are much more sensitive to electronic effects than those of the iridium complexes. However, the energy calculations at the RHF//RHF level for M = Rh and at the MP2//RHF for M = Ir give reasonable relative energies, which are in general agreement with the calculated results at the MP2//MP2 and MP4SDQ//MP2 levels. At the RHF level, all models agreed with the thermodynamic preference for the η^2-pyrazolylborate η^2-ethene species in the rhodium compounds, with exothermicities from −20 to −28 kcal/mol and a barrier of about 12 kcal/mol. For the iridium complexes, in most cases the system favors an η^3-pyrazolylborate η^2-ethene structure with a exothermicities from −2 to −10 kcal/mol. However, with an increase of the steric effect of the pyrazolyl group, as found in model **g**, the isomerization of the iridium η^3-pyrazolylborate η^2-ethene complexes to hydridovinyl complexes becomes exothermic by −6.3 to −0.8 kcal/mol at the RHF//RHF and MP2//RHF levels, respectively.

In complexes without strong steric effects, the M(I)−(η^2-ethene) → M(III)−(hydridovinyl) reaction is generally more endothermic for Rh than Ir. This electronic preference is a reflection of the preference for late second-row transition metals to have d^{n+1} ground states with high-lying d^{n}s^1 excited states, while late third-row transition metals have either d^{n}s^1 ground states or d^{n}s^1 low-lying excited states. Thus, the third-row transition metal undergoes oxidation−addition more easily than its second-row transition metal congener.