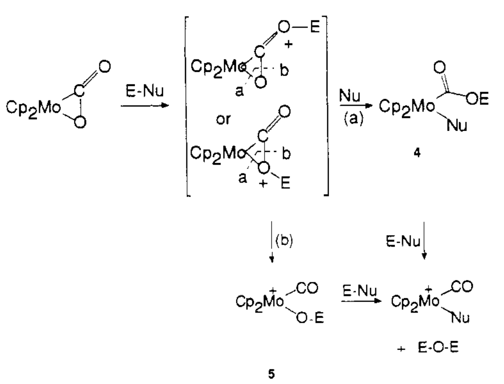
Scheme II



assignment, its X-ray crystal structure was determined[13] and is presented in Figure 1. Besides the expected cyclopentadienyl and carbonyl ligands of **3**, a THF molecule was found to be coordinated in place of the weakly donating triflate, providing the first example of a dicationic $Cp_2M(CO)L$ complex.[14] In each of these reactions of **1** cleavage of coordinated CO_2 to CO has occurred with oxygen transfer to the electrophilic silicon atom.

Similar CO_2 "splitting" resulted from the interaction of **1** with H^+ as the electrophile. Thus, when a CH_2Cl_2 solution of **1** was treated with excess HCl(g) at −78 to −20 °C, the chloro carbonyl complex **2a** was again produced (>50%) in addition to H_2O, which could be detected by ^1H NMR spectroscopy (Scheme I) and verified by spiking. This reaction constitutes a stoichiometric "reverse" water-gas shift reaction, i.e. $CO_2 + 2e^- + 2\,H^+ \rightarrow CO + H_2O$, with the electrons being supplied by Mo.

The reactivity of **1** toward some carbon electrophiles also was briefly surveyed. No reaction was observed when **1** was treated with CH_3I in THF at 0 °C. On the other hand, $CH_3OSO_2CF_3$ (2 equiv) reacts rapidly with **1** under the same conditions to afford an inseparable mixture of products, including CO_2-cleavage $[(C_5H_5)_2Mo(CO)Z]^+$ derivatives **2b** (ν_{CO} 2050 cm⁻¹). Carboxylic acid chlorides, including oxalyl, acetyl, and 4-nitrobenzoyl chlorides (2 equiv), were found to react slowly with **1** in CH_2Cl_2 during warming from −78 to 0 °C. The major product isolated (30%) from the reaction with oxalyl chloride proved to be the carbonyl chloride salt **2a**. On the other hand, addition of pentane to the $1/CH_3C({=}O)Cl$ reaction mixture caused precipitation of a mixture of **2a**, $CpMoCl_2$, and the acetato carbonyl complex **2c** (Scheme I) as judged by IR, ^1H NMR, and MS analysis.[15]

The Lewis acids $BF_3{\cdot}Et_2O$ and BCl_3 also were found to induce (rapid) CO_2 splitting in **1** (2 equiv, −78 °C, CH_2Cl_2 or THF), producing cationic carbonyl salts. The product from the reaction with BCl_3 (79%) was identified once again as the carbonyl chloride salt **2a**. The nature of the inner- and outer-sphere ions of the very sensitive BF_3-derived product, however, cannot be identified with certainty at present.[16]

Finally, some oxophilic but less electrophilic reagents were found to be unreactive toward **1**. Thus, neither $Me_3SiSiMe_3$ nor PPh_3 reacted with **1** below 0 °C; at higher temperatures decomposition of **1** to the recently characterized $(C_5H_5)_2Mo(\eta^2\text{-}CO_3)$[7] occurred.

Two mechanisms that account for the observed electrophilic cleavage of coordinated CO_2 in **1** are suggested in Scheme II. Initial attack by the electrophile (i.e. R_3Si^+, H^+, R^+, RCO^+, BX_3) could occur on either the coordinated or noncoordinated oxygen atom of CO_2. Subsequent scission of the Mo–O bond (pathway a) would give the metallocarboxylate derivative **4**, whereas C–O scission would lead to the cationic carbonyl species **5**. Either **4** or **5** then could react rapidly with a second equivalent of the reagent to produce the final product **2**. At present we cannot unambiguously distinguish between pathways a and b. Use of 1 equiv of reagent (e.g. with R_3SiX) generally afforded only product complex **2** and starting CO_2 complex **1**. Furthermore, IR monitoring at room temperature of several reactions failed to detect any intermediate species. However, low-temperature (−30 °C) ^1H NMR (CD_2Cl_2) monitoring of the reaction between **1** and $^tBuMe_2SiCl$ revealed transient C_5H_5– (5.15 ppm), $(CH_3)_3C$– (0.75 ppm), and $(CH_3)_2Si$– (0.07 ppm) resonances, which are appropriately positioned for a neutral intermediate such as **4** (E = $^tBuMe_2Si$). Efforts are underway to identify these intermediates and to explore further the reactions of **1** with external reagents.

Acknowledgment. We are grateful for support provided by the U.S. Department of Energy under Grants DE-FG01-87FE61146 and DE-FG05-89ER13997 (Office of Basic Energy Sciences, Division of Chemical Sciences).

Supplementary Material Available: Listings of atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, and torsion angles for **3** (7 pages); a listing of structure factors (7 pages). Ordering information is given on any current masthead page.

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[13] X-ray crystal data for **3**: molecular formula $C_{17}H_{18}F_6MoO_8S_2$; M_r = 624.38; orthorhombic space group $P2_12_12_1$; a = 18.518 (4) Å, b = 15.773 (4) Å, c = 7.353 (2) Å, V = 2147.7 Å³; Z = 4; μ(Mo Kα) = 7.89 cm⁻¹; R = 0.086, R_w = 0.096 for 1672 unique relections, ρ_{max} in the final difference map 7.6 e Å⁻³. Data were collected at 160 ± 2 K with an Enraf-Nonius CAD4 diffractometer with monochromated Mo Kα (0.71069 Å) radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares method. Poor crystal quality, however, limited the data quality, the main reason for the high R factor and the low accuracy of the structural parameters. Unusually, the highest peak in the difference map (7.6 e Å⁻³) was found at 0.95 Å from the Mo atom. The location of this peak is too close to Mo and O(2) to be a bonded atom. Because of its unusual height the possibility of a disordered Mo position was checked, but it did not lead to a meaningful refinement. All of the interionic contacts are normal, the shortest (3.03 (2) Å) being between F(3) of $CF_3SO_3^-$ and C(5). Despite this peculiarity the gross molecular structural features of **3** are secure.

[14] A small number of $[Cp_2MoLL']^{2+}$ salts have been prepared, all of which have L and L′ as N- or P-donors: Calhorda, M. J.; Diaz, A. R. *Rev. Port. Quim.* **1981**, *23*, 12. Calhorda, M. J.; Diaz, A. R. *J. Chem. Soc., Dalton Trans.* **1980**, 1443. Aviles, T.; Green, M. L. H.; Diaz, A. R.; Romao, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1367. Forder, R. A.; Gale, G. D.; Prout, K. *Acta Crystallogr., Sect. B* **1975**, *31*, 297.

[15] Spectroscopic data for $[Cp_2Mo(CO)OCOCH_3]Cl$ (**2c**, admixed with Cp_2MoCl_2 and **2a**): IR (KBr) 2050, 1645 cm⁻¹; ^1H NMR (acetone-d_6) δ 6.46 (s, 10 H), 2.09 (s, 3 H); MS (FAB) m/e 351.0 ($Cp_2{}^{98}Mo(CO)OCOCH_3^+$, 54), 286.9 ($Cp_2{}^{98}MoOCOCH_3^+$, 86), 255.9 ($Cp_2{}^{98}MoCO^+$, 14), 228.0 ($Cp_2{}^{98}Mo^+$, 37).

[16] Spectroscopic data for the product from **1** + $BF_3{\cdot}Et_2O$: IR (KBr) 2070 cm⁻¹; ^1H NMR (acetone-d_6) δ 6.53 (C_5H_5); ^{19}F NMR (acetone-d_6, CF_3CO_2H reference) δ −103.7; MS (FAB) m/e 434.9, 403.1, 337.0, 256.0 ($Cp_2{}^{98}MoCO$), 244.0 ($Cp_2{}^{98}MoO$), 228.0 ($Cp_2{}^{98}Mo$, 100).

Nucleophilic Addition to Coordinated Imines: Diastereoselective Synthesis of the Ruthenium Amide Complexes $(\eta^6\text{-}C_6Me_6)RuN(Ph)CRR'C_6H_4(PMe_3)$

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Received April 10, 1989

Summary: The complex $(\eta^6\text{-}C_6Me_6)Ru(PMe_3)Cl_2$ reacts with 2 equiv of benzylideneaniline and 2 equiv of $[Ag][BF_4]$ to give the cationic ortho metalated imine complex

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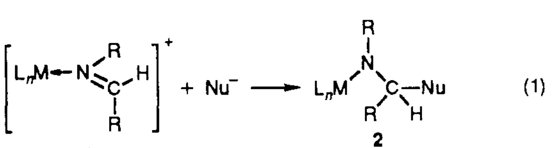
$[(\eta^6\text{-}C_6Me_6)Ru{\leftarrow}N(Ph){=}C(H)C_6H_4]^+$. Strong nucleophiles ($R^-$, H^-) add to the imine carbon to give the amide complex $(\eta^6\text{-}C_6Me_6)RuN(Ph)C(H)(R)C_6H_4$, which is formed with ca. 100% diastereoselectivity in a kinetically controlled addition reaction.

We have been interested in the synthesis of late-transition-metal amide complexes because of their possible use in C–N bond-forming reactions. These compounds have most frequently been synthesized by metathetical exchange of a halide or other leaving group with an alkali-metal amide.[1] This method, although useful for some compounds, can suffer from undesirable side reactions such as reduction of the metal or deprotonation of the ancillary ligands. It is possible that amide complexes of metals such as ruthenium are uncommon due to a lack of viable synthetic procedures rather than because of thermodynamic instability of the $M\text{-}NR_2$ bond. Recent studies indicate that when such compounds can be made, they are at least moderately stable.[1e,2] Thus, we have begun examining alternative routes to such compounds in order to facilitate the development of their chemistry.

One possible synthetic procedure that has attracted our attention exploits the enhanced electrophilicity of the carbon atom of an imine that is coordinated to a transition-metal cation. Attack of a nucleophile at the coordinated imine as shown in eq 1 will lead to the formation



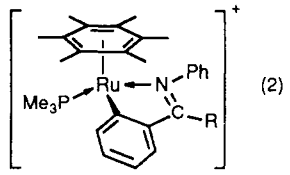
1 2

of the desired amide complex 2. Enhancement of the electrophilicity of imines through coordination to Lewis acids has been successfully employed in the synthesis of allylic amines,[3,4] and enhancement of the electrophilicity of aldehydes and ketones by Lewis acid coordination is well-known.[5]

Although monodentate N-bound imine complexes are rare as a result of the weak Lewis basicity of the imine nitrogen,[6] the ortho metalated benzylideneaniline complex **4a** is readily prepared from **3** in 80% yield as a yellow crystalline solid as shown in eq 2. Compound **4a** has been

$(\eta^6\text{-}C_6Me_6)RuCl_2PMe_3 + 2AgBF_4 + 2PhN{=}C(R)Ph \longrightarrow$

3



4a, R = H
b, R = CH_3

characterized spectroscopically,[7a,b] and the presence of the ortho metalated benzylideneaniline group is confirmed by ^1H COSY NMR spectroscopy.[8] Ortho metalated complexes of Schiff bases and other N donor ligands that are related to 4 are well-known, and their chemistry has been reviewed.[9] Since **4a** contains an imine coordinated to a

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(7) (a) A solution of **3** and benzylideneaniline was allowed to react with a suspension of 2 equiv of $[Ag][BF_4]$ in CH_2Cl_2 for 12 h. The resultant yellow solution was filtered and the CH_2Cl_2 removed under reduced pressure. Washing with pentane, ether, and THF gave **4a** as yellow microcrystals. The second equivalent of imine in eq 2 was converted to $[Ph(H)N{=}C(H)Ph]^+$. (b) Compound **4a**: Anal. Calcd for $C_{28}H_{37}BF_4NPRu$: C, 55.4; H, 6.15; N, 2.31. Found: C, 55.2; H, 6.25; N, 2.29. Mp 280–282 °C. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): δ 8.33 (d, $J_{P\text{-}H}$ = 2.9 Hz, 1 H, imine H), 7.66 (d, J = 8.4 Hz, 1 H, ring), 7.52 (d, J = 8.1 Hz, 1 H, ring), 7.46 (t, J = 8.4 Hz, 2 H, aniline), 7.33 (t, J = 7.2 Hz, 1 H, aniline), 7.25 (d, J = 8.1 Hz, 2 H, aniline), 7.19 (t, J = 8.1 Hz, 1 H, ring), 7.04 (t, J = 7.8 Hz, 1 H, ring), 1.80 (s, 18 h, $C_6\mathit{Me}_6$), 1.07 (d, J = 9.1 Hz, 9 H, $P\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (74.4 MHz, $CDCl_3$, 22 °C): δ 187.0 (d, J = 21.7 Hz, imine C), 175.3, 151.3, 146.5, 137.7, 131.2, 130.5, 129.9, 128.6, 123.2, 121.9 (aniline and ring), 102.85 (d, $J_{P\text{-}C}$ = 2.4 Hz, C_6Me_6), 15.72 (C_6Me_6), 14.80 (d, J = 32.9 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 22 °C): δ 7.60. Compound **4b**: Anal. Calcd for $C_{29}H_{39}BF_4PRu$: C, 56.1; H, 6.34; N, 2.26. Found: C, 55.9; H, 6.40; N, 2.22. Mp 271–273 °C. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): δ 7.58–7.50 (m, 4 H, ring and aniline), 7.32 (t, J = 6.5 Hz, 1 H, ring or aniline), 7.25 (t, J = 7.8 Hz, 1 H, ring or aniline), 7.12 (t, J = 7.4 Hz, 1 H, ring or aniline), 7.01 (d, J = 7.9 Hz, 2 H, aniline), 2.39 (d, $J_{P\text{-}H}$ = 1.5 Hz, 3 H, imine Me), 1.81 (s, 18 H, $C_6\mathit{Me}_6$), 1.11 (d, J = 9.23 Hz, 9 H, $P\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ 184.7 (d, J = 22 Hz, imine C), 180.4, 150.3, 147.8, 137.8, 130.5, 129.5, 129.1, 127.7, 123.6, 122.9 (ring or aniline), 103.0 (C_6Me_6), 18.2 (imine Me), 15.7 ($C_6\mathit{Me}_6$), 14.9 (d, J = 32.7 Hz, $P\mathit{Me}_3$). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 22 °C): δ 2.705. Compound **5a**: Anal. Calcd for $C_{28}H_{38}NPRu$: C, 64.6; H, 7.35; N, 2.69. Found: C, 64.5; H, 7.38; N, 2.74. Mp 132–136 °C dec. ^1H NMR (300 MHz, C_6D_6, 22 °C): δ 7.42 (t, J = 6.6 Hz, 1 H, phenyl), 7.28 (t, J = 8.4 Hz, 1 H, phenyl), 7.21 (t, J = 5.1 Hz, 1 H, phenyl), 7.18–7.08 (m, 3 H, phenyl), 6.76 (t, J = 8.7 Hz, 1 H, phenyl), 6.57 (t, J = 6.9 Hz, 1 H, phenyl), 6.47 (d, J = 8.1 Hz, 1 H, phenyl), 4.75 (d, $J_{H\text{-}H}$ = 16.5 Hz, 1 H, benzylic H), 4.47 (d of d, $J_{H\text{-}H}$ = 16.5, $J_{P\text{-}H}$ = 3.3 Hz, 1 H, benzylic H), 1.62 (s, 18 H, C_6Me_6), 0.78 (d, J = 8.7 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 22 °C): δ 159.0, 153.3, 137.9, 129.6, 127.5, 124.2, 122.0, 121.3, 120.3, 119.6, 112.3, 108.3 (aromatic C), 99.6 (C_6Me_6), 82.8 (benzylic C), 16.4 (d, J = 29.4 Hz, $P\mathit{Me}_3$), 16.2 ($C_6\mathit{Me}_6$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 22 °C): δ 7.54. Compound **5b**: Anal. Calcd for $C_{29}H_{40}NPRu$: C, 65.1; H, 7.54; N, 2.62. Found: C, 64.8; H, 7.51; N, 2.59. Mp 203–205 °C dec. ^1H NMR (300 MHz, C_6D_6, 22 °C): δ 7.64 (t, J = 8.4 Hz, 1 H ring), 7.52 (t, J = 7.2 Hz, 1 H, ring), 7.41–7.30 (m, 5 H, ring and aniline), 7.14 (d, J = 8.1 Hz, 1 H, ring), 6.82 (t, J = 7.5 Hz, 2 H, aniline), 5.01 (d of d, $J_{H\text{-}H}$ = 5.67 and $J_{P\text{-}H}$ = 2.47 Hz, 1 H, benzylic H), 1.78 (d, J = 5.7 Hz, 3 H, –CH*Me*–), 1.94 (s, 18 H, $C_6\mathit{Me}_6$), 0.93 (d, J = 9.0 Hz, 9 H, $P\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (74.4 MHz, C_6D_6, 22 °C): δ 158.4, 138.4, 130.8, 129.5, 129.0, 124.1, 122.3, 121.1, 121.0, 112.0, 108.3, 99.5 (ring and aniline C), 68.0 (benzylic C), 24.3 (Me), 16.5 ($C_6\mathit{Me}_6$), 16.0 (d, J = 30.0 Hz, $P\mathit{Me}_3$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 22 °C): 8.977. Compound **5c**: ^1H NMR (300 MHz, C_6D_6, 22 °C): δ 7.31–7.19 (m, 2 H, ring or aniline), 7.16–7.12 m, 2 H, ring or aniline), 7.08–7.02 (m, 2 H, ring or aniline, 6.83 (d, J = 6.9 Hz, 1 H, ring or aniline), 6.67 (d, J = 5.4 Hz, 1 H, ring or aniline), 6.53 (t, J = 6.9 Hz, 1 H, ring or aniline), 5.15 (q, J = 5.7 Hz, 1 H, benzylic H), 1.56 (d, J = 5.7 Hz, 3 H, benzylic Me), 1.51 (s, 18 H, $C_6\mathit{Me}_6$), 0.93 (d, J = 8.7 Hz, 9 H, $P\mathit{Me}_3$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 22 °C): δ 4.16. Compound **5d**: Anal. Calcd for $C_{34}H_{42}NPRu$: C, 68.4; H, 7.09; N, 2.35. Found, C, 68.1; H, 7.13; N, 2.31. Mp 145–148 °C dec. ^1H NMR (300 MHz, C_6D_6, 22 °C): δ 7.78–7.75 (m, 2 H, aromatic), 7.28–7.21 (m, 4 H, aromatic), 7.17–7.07 (m, 6 H, aromatic), 6.53 (t, 8.1 Hz, 1 H, ring or aniline), 5.97 (s, 1 H, benzylic H), 1.59 (s, 18 H, $C_6\mathit{Me}_6$), 0.64 (d, J = 9.0 Hz, 9 H, $P\mathit{Me}_3$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 22 °C): δ 7.92. (c) A solution of the appropriate alkyllithium was added to a THF suspension of **4a,b** at −20 °C. Within ca. 15 min the suspended solid dissolved to give an organic solution. The THF was removed under reduced pressure and the resultant residue extracted with pentane. Concentrating and cooling the combined pentane extracts gave **5a–d** as orange crystals.

(8) ^1H COSY and difference proton NOE spectra are supplied as supplementary material.

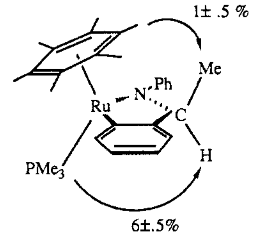
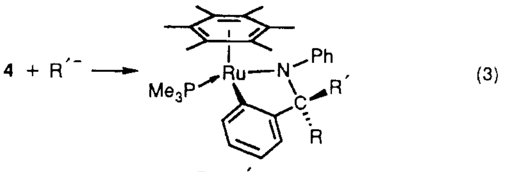


Figure 1. Proposed structure of **5b** showing observed ^{1}H NOE enhancements. Within experimental error, irradiation of the C_6Me_6 protons does not enhance the benzylic proton, and irradiation of the PMe_3 protons does not enhance the benzylic methyl group.

metal cation, the imine carbon in **4a** should be susceptible to nucleophilic attack, giving an ortho metalated benzylphenylamide as the product. Related metallocycles, containing both M-aryl and M-O(σ) bonds, have been synthesized by the reaction of 2-carboxylatobenzenediazonium or 2-sulfonatobenzenediazonium with low-valent platinum complexes.[9f]

When **4a** is allowed to react with 1 equiv of Li(t-BuO)$_3$AlH (THF, −20 °C), an immediate reaction occurs, producing the orange pentane-soluble product **5a** in ca. 95% yield:



5a, R = R′ = H
b, R = H, R′ = CH$_3$
c, R = CH$_3$, R′ = H
d, R = H, R′ = Ph

The ^{1}H NMR spectrum of **5a** has a pair of doublets at 5.5 and 4.5 ppm that are assigned to the benzylic protons which are diastereotopic. The remainder of the ^{1}H NMR spectrum (as well as the ^{13}C and ^{31}P spectra) is also consistent with the proposed structure of **5a**.[7b] Other strong nucleophiles such as lithium alkyls will also add to the imine carbon to give **5b–d**.[7b]

If the attacking nucleophile is different from the substituent already bonded to the imine carbon, then the formation of two sets of diastereomers is possible since both the Ru center and the benzylic carbon atom are chiral. When MeLi is added to a solution of **4a** in THF, only one product, **5b**, is observed by 300-MHz ^{1}H NMR spectroscopy following workup. The structure of **5b** has been assigned with the aid of proton difference NOE spectroscopy and is shown in Figure 1 along with the observed NOE(s). Thus, **5b** is formed with ca. 100% diastereoselectivity. The other diastereomer, **5c**, can be synthesized by adding Li(t-BuO)$_3$AlH to **4b** followed by rapid workup of the reaction mixture. Under these conditions, **5c** is the only detectable product of the reaction. These experiments demonstrate that both methyl addition to **4a** and hydride addition to **4b** occur endo to the C_6Me_6 ring rather than between the "legs" of the piano stool. If compound **5c** is allowed to remain in solution, a slow isomerization ($t_{1/2} \simeq$ 18 h, 25 °C) occurs that converts it cleanly and completely to **5b**. This leads to the conclusion that while the regioselectivity of the nucleophilic attack is kinetically controlled and occurs endo to the C_6Me_6 group, **5b** is the thermodynamically more stable isomer of the pair of diastereomers (**5b** and **5c**).

Preliminary kinetic studies have been carried out on the isomerization of **5c** to **5b**. The reaction is first order in **5c**, and the activation parameters[10] are consistent with a considerable amount of bond breaking in the transition state. A mechanism involving loss of PMe_3 to form an unsaturated 16e intermediate that can trap PMe_3, resulting in a net racemization of the ruthenium center, would be consistent with these results. Since there are no examples of such racemization reactions that occur in complexes with ortho metalated ligands,[10] further studies are underway to elucidate the mechanism of this reaction in more detail.

The observation that nucleophilic attack occurs at the imine carbon of **4a,b** to give amide complexes demonstrates the viability of eq 1 as a method for the synthesis of metal amide complexes. The extraordinarily high diastereoselectivity of H$^-$ or R$^-$ addition to the imine carbon is reminiscent of the selectivities observed in reactions occurring at ligands coordinated to other three-legged piano-stool complexes.[11] We are currently exploring the generality of this reaction with other ortho metalated Schiff base complexes since the syntheses of monodentate amido complexes by this chemistry have not yet been successful. Results of studies on the reactions of **5b** with acetylene, carbon monoxide, and other unsaturated reagents will be reported separately.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: A ^{1}H COSY NMR spectrum for $(\eta^6\text{-}C_6Me_6)\overline{Ru{\leftarrow}N(Ph){=}C(H)C_6H_4}(PMe_3)$ (**4a**) and ^{1}H difference NOE spectra for $(\eta^6\text{-}C_6Me_6)\overline{RuN(Ph)C(H)(Me)C_6H_4}$ (isomer **5b**) (2 pages). Ordering information is given on any current masthead page.

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Ab Initio MO Study of CO_2 Insertion into a Cu^I–CH_3 Bond. Critical Difference from CO_2 Insertion into a Cu^I–H Bond

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Received May 31, 1989

Summary: Several interesting differences are found between CO_2 insertion into a Cu^I–CH_3 bond and CO_2 insertion into a Cu^I–H bond, which come from the fact that an alkyl ligand possesses only a directional lone-pair orbital as a valence orbital while the hydride ligand has a spherical 1s orbital as a valence orbital.